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北海道南部に於ける淡水産カジカ類に就いて

佐藤信一（水産動物第一教室）
小林喜雄（同上）

A NOTE ON THE FRESH WATER COTTOID FISHES IN SOUTHERN HOKKAIDO.

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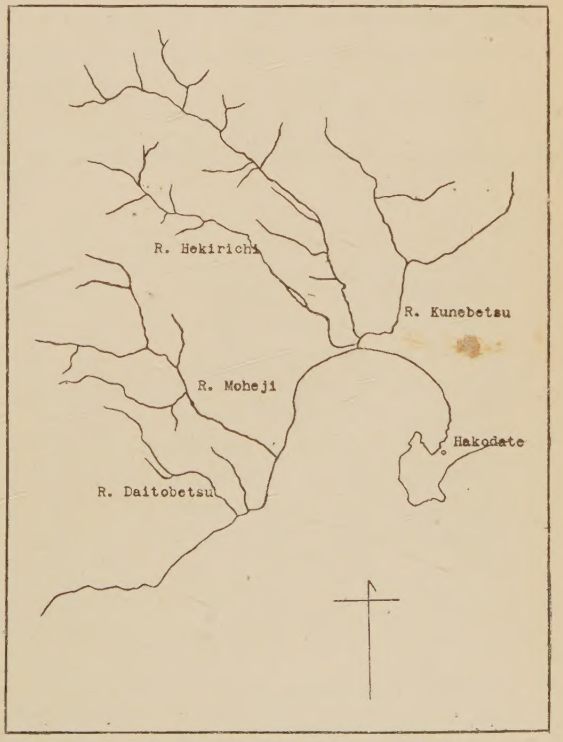
(Faculty of Fisheries ,Hokkaido University,Hakodate)

In the present paper two species of the fresh water cottoid fishes, *Cottus nozawae SNYDER* and *Cottus hangiongensis MORI*, have been studied from the taxonomical point of view.

C. nozawae SNYDER is rather commonly found in the rivers of Hokkaido, usually in the middle and upper courses of the stream.

C. hangiongensis MORI has not been yet found in the rivers of Japan, only reported from the middle courses of the Tumenula River in northern Korea by Mori ('30). Since 1947, we have collected 31 specimens of the latter in the lower courses of the Daitobetsu, Moheji and Hekirichi Rivers, and some ecological observations have been also carried on.

Fig. 1. The map of the rivers in southern Hokkaido.



北海道の各河川に棲息するカジカ類については Günther ('73) が小樽内川で採集した個體について *Cottus pollux GüNTHER* と命名し、其の後 Jordan 及び Starks ('04) が本州に廣く分布する *Cottus hilgendorfi STEINDACHNER* を C. pollux の synonym とし、本州に於けるカジカと同種と見なしていた。Snyder ('11) は石狩川より更に *C. nozawae SNYDER* を報告し、北海道には2種が棲息すると一般に考えられていたが、實際には普通に見られるのは *C. nozawae* のみであつて、其の後 *C. pollux* を採集した記載は無い。岡田及び池田 ('38) は *C. pollux* はこの種は北海道では稀であつて恐らく日本海に面する北海道南部に限られているのではないか

と述べている。筆者等はこの2種の實際の分布狀態を確めるために1947年以降北海道の南部に於ける河川、本州北端の青森縣の河川を調査した。採集は主として知内川、大當別川、茂邊地川、戸切地川、久根別川等の河川で（Eig. 1）約70個體を得、これ等を觀察した結果 *C. pollux* に相當するものは一個體も無く、むしろ從來吾國で知られなかつた *C. hangiongensis MORI* に相當するものを31個體見出したので、その形態並びに生態の一部を報告する。

猶この調査には文部省科學研究費を使用した。

1 *Cottus nozawae SNYDER*

ハ ナ カ ジ カ

本種は前に述べた様に Snyder ('11) が石狩川より最初に記載して以來、北海道の各地で採集され南千島及び南樺太にも棲息することが知られている (Sato, '42)

觀察した個體は主として茂邊地川、久根別川、及び戸切地川より採集した28個體で、全長48～193 mm（體長39～162mm）の大さのものである。

形 態. (Table. 1.)

D. Ⅷ—Ⅹ, 17～20; A. 13～15; P. 14～16; V. I, 4.

體長は頭長の2.68～3.31倍、頭長は尾柄高の3.18～4.52倍、吻長の2.82～3.62倍、上顎長の1.83～2.59倍、眼經の3.64～6.79倍、鰓耙數は $\frac{0+3\sim5}{0\sim1+4\sim7}$、鰓蓋前骨棘は3本、口蓋骨には齒がない。背椎骨は35～36.

成體では胸鰭後緣はは肛門の位置に迄達している。胸鰭軟條は上部の1～2條を除き、それに續く4～8條が分枝している。腹鰭は雄ではその內側面に疣狀突起が見られる。肛門の位置は常に體の中央より稍々後方で、吻端より肛門までの長さは體長の51.4～58.8% を示している。

Table 1. Measur ements of *Cottus nozawae SNYDER.*

Locality	Kunebetsu River	Hekirichi River	Moheji River
Number	1	21	6
Total length	150 mm	193— 48 mm	192— 83 mm
Body length	127 mm	162— 39 mm	161— 69 mm
Depth of body in body length	4.22	4.49—3.62	4.57—3.84
Head length in body length	2.85	3.31—2.82	3.09—2.68
Depth of caudal peduncle in head length	4.46	4.30—3.18	4.52—3.72
Length of snout in head length	3.51	3.62—2.86	3.37—2.82
Length of maxillary in head length	2.37	2.50—1.87	2.59—1.83
Interorbital space in head length	6.19	7.06—4.27	6.54—4.37
Diameter of eye in head length	4.96	6.79—3.64	6.09—4.66
Number of spines of D.	VIII	VIII—IX	VIII—X
rays of D.	19	17— 20	18— 19
P.	15	14— 16	15— 16
A.	15	13— 15	13— 15
V.	I, 4	I,4	I,4
Number of gill rakers	$\frac{0+4}{1+5}$	$\frac{0+4-5}{0-1+6-7}$	$\frac{0+3-4}{1+4-6}$
Number of vertebrae		12+23—24	

別表に示す如く本州産の *C. pollux GüNTHER* に比較して背鰭軟條及び臀鰭軟條の多いこと、胸鰭に分枝軟條のあること、鰓蓋前骨棘が3本であること等で明に區別し得る。岡田及び中村('48)は *C. nozawae SNYDER* を *C. reinii HILGENDORF* の synonym と見なしているが、筆者等は *C. reinii* に相當する個體は未だ見出し得ず、むしろ Schmidt ('04) が南樺太の Lutoga River (留多加川) より記載し、沿海州の日本海側の河川に廣く分布する。*C. amblystomopsis SCHMIDT* との間に近緣關係があるのではないかと考えられる、このことは Taranetz ('36) も同様に考えている様で、更に今後樺太及び千島、北海道各地の個體について考究する豫定である。

棲息狀態

この類の生態については先に岡田氏 ('36) が千歳川のものについて產卵習性を述べている。但し *C. pollux GüNTHER* の種名を用いているが、其の後の筆者等の調査に依り *C. nozawae SNYDER* であることが明にされた。前述の各河川での棲息範圍は廣く、河口近くより上流及び各支流にまで棲息する。勿論河川の河口の形狀等に依り多少の差はあるが、茂邊地川で殆ど海水の混入する區域との限界附近まで達している。全長約 150mm 以上の大型のものは河流中特に〝溜り〟のある岸邊の土中の穴に棲息することが、春季茂邊地川及び戸切地川で見られた。これに反し小型のものは比較的流れの早い所に棲息し、その範圍も廣い。

2 *Cottus hangiongensis MORI*

本種は森 ('30) 氏に依り朝鮮の開寧より初めて報告されたもので、現在まで吾國に於て記載されなかつたものである。觀察に用いた個體は1947年以降茂邊地川、大當別川及び戸切地川で採集された、全長60～148mm (體長50～127mm)、31個體である。

形態. (Table 2.) (Fig 2.)

D. Ⅶ—Ⅸ, 20—22; A. 14～16; P. 13～14; V. I, 4.

體長は頭長の3.17～3.70倍、頭長は尾柄高の2.66～3.48倍、吻長の2.88～3.87倍、上顎長の1.74～2.64倍、眼徑の3.55～4.90倍、鰓耙數は$\frac{0+4\sim6}{0\sim1+7\sim10}$、鰓蓋前骨棘は1本、口蓋骨に齒はない。背椎骨數は36～37個。

Table 2. Measurements of *Cottus hangiongensis MORI*

Locality	Daitobetsu River	Hekirichi River	Moheji River
Number	1	15	19
Total length	94 mm	148— 63 mm	122— 60mm
Body length	80 mm	127— 54 mm	103— 50mm
Depth of body in body length	6.82	7.52—4.11	5.51—4.30
Head length in body length	3.53	3.70—3.30	3.61—3.17
Depth of caudal peduncle in head length	3.48	3.25—2.66	3.41—2.72
Length of snout in head length	3.48	3.57—2.92	3.872—.88
Length of maxillary in head length	2.20	2.63—1.74	2.64—1.94
Interorbital space in head length	7.32	8.30—5.98	7.73—6.07
Diameter of eye in head length	3.98	4.90—3.71	4.30—3.55
Number of spines of D.	VIII	VIII—IX	VIII
rays of D.	21	20—22	21—22
P.	14	13—14	14
A.	16	14—16	14—16
V.	I.4	I.4	I.4
Number of gill rakers	$\frac{0+5}{0+8}$	$\frac{0+4-6}{0-1+7-10}$	$\frac{0+5-6}{0-1+7-8}$
Number of vertebrae		11—12+25	11—12+25

成體では胸鰭は肛門に達する。體の背側は黒褐色で小黒點が散在する。腹側は淡褐色か白色である。尾柄の背腹兩側に眼徑大の黒斑がある。約100mm以下の大きさのものでは體は淡褐色で、極めて不明瞭な4條の横帶があり、尾柄の褐色斑は明瞭である。背鰭、臀鰭には明瞭な2～3條の褐色帶があり、胸鰭、腹鰭、尾鰭には7～8條の褐色帶がみられる。一般成體の雄では肛門突起は顯著であるが、雌では殆ど認められ無い。また *C. nozawae* の雄に見られる腹鰭内側の疣狀突起は全く現れない。肛門の位置は體の殆ど中央か或は多少後方による。吻端より肛門迄の距離は體長の48.3～55.2%である。それ故他の種類を比較して見ると、*C. nozawae* よりは背鰭及び臀鰭軟條が多く、胸鰭軟條は少い、また分枝軟條が見られない。鰓蓋前骨棘が1本であること、鰓耙數、背椎骨がいづれも多いことで區別される。

C. pollux とは背鰭及び臀鰭軟條の多いこと、胸鰭軟條の少いこと、鰓耙數並に背椎骨數で異る。

C. kazika JORD. & ST. とは頭長、背鰭並に臀鰭軟條數、鰓蓋前骨棘が異り、特に口蓋骨に齒の無いことで明に區別される、その點については體型はよく似ていて沿海州を分布する *C. czerskii* とも同樣に區別し得る。

Berg ('31) はこの *C. hangiongensis* は *C. amblystomopsis* と非常によく似ているが背鰭及び臀鰭軟條數が多いと述べ、Taranetz ('36) はこれ等の2種は Synonym ではないかと考えているが、同時に *C. nozawae* についても同樣な意見を示している。筆者は前述の如く *C. amblystomopsis* と *C. nozawae* の間には近緣關係は認められるが、*C. nozawae* とは明かに區別しうる。

むしろ胸鰭の特徴よりして *C. pollux* と *C. nozawae* の中間型を示すものである。

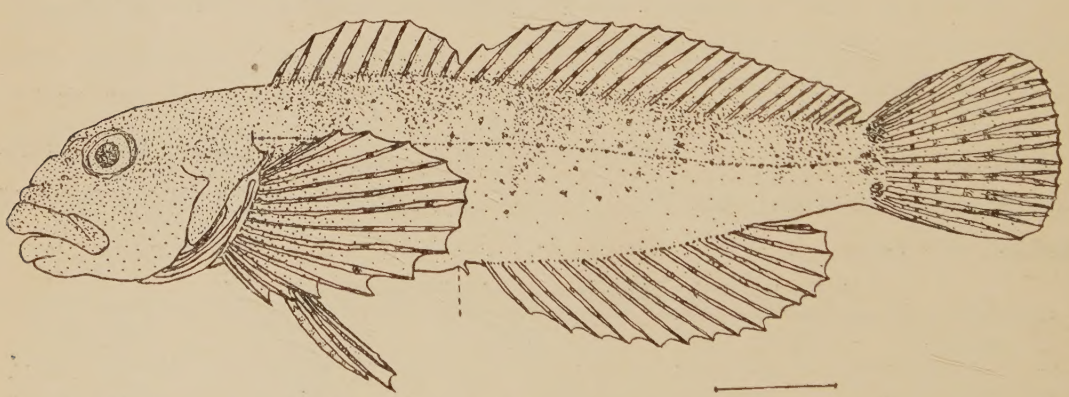


Fig 2. *Cottus hangiongensis MORI*
♂, 87 mm in total length, Hekirichi River.

棲息狀態並に分布

この種類は *C. nozawae* と異り、その棲息する範圍は各河川の下流附近に限られている。ことに春期5月の産卵期にはその現象が明かで、戸切地川では河口より約2粁、茂邊地川では約1粁附近を上限として産卵し、それより上流には殆ど棲息しない。これは同じ河川で、殆ど同時期に *C. nozawae* が河口より8～10粁以上の上流で産卵し、産卵場所の明に區別しうることからも推察される。猶、産卵習性並に發生に關しては次の機會に述べる豫定である。

分布狀況は現在のところ不明な點が多いが、筆者等が先に石狩川河口附近の厚田川より採集された ('36. VII. 17) 8個體を觀察しているので、北海道の日本海沿岸の河川には相當廣く分布すると考えられる。

摘　　要

1947年以降、北海道の南部の河川、即ち大當別川、茂邊地川、戸切地川及び久根別川等よりカジカ2種を採集し、次の事を觀察した。

1. 從來北海道の各河川に分布すると云はれる *C. nozawae SNYDER* 及び *C. pollux GüNTHER* の2種のうち *C. pollux* に相當するものは1個體も見出し得なかつた。

2. *C. nozawae SNYDER* は本州産の *C. pollux GüNTHER* と明に形態的に相異し、道南の河川の上流より河口近くまで廣く棲息するが、一般に中流以上に多い。

3. 森('30) 氏に依つて豆滿江より記載された *C. hangiongensis MORI* に相當する、31個體を大當別川、茂邊地川、戸切地川より採集し得た。この種は各河川の下流に棲息し且産卵する。

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（水產科學研究所業績 第58號）

流氷中のプランクトンの觀察

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OBSERVATION OF THE PLANKTON IN DRIFT ICE.

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Present author observed the planktons in the blocks of drift ice in the neighbouring waters of Abashiri and Nemuro (Hokkaido).

I have found that each block of drift ice contains in it various kinds of planktons and these planktons show a slight difference in the kind and the composition from those in the sea water where the very ice blocks are collected. This fact will certainly suggest that the observation of the planktons in drift ice furnishes the data to presume various matters in the field of oceanography and meteorology–where the ice block froze, its course and speed of drifting, temperature at the freezing time (to be presumed by the thickness of the ice block), etc.

1　緒　　言

寒海で海水が結氷する際には表面の海水中に含れてゐるプランクトンは氷の中に包藏されるが、春季氣溫が幾分上昇し風浪その他の營力が作用すると全面的に結氷は破碎され、旦流氷となつて風及び海流によつて漂流を始める。この流氷中に含有されるプランクトンの種類及び組成の狀態を調査することは結氷海區や流氷の經路分布等を推定する資料として重要性がある。流氷中に含まれるプランクトンに就ての研究は少くて嘗つて松平氏（1932）が根室沖で採集した流氷中から檢鏡したことがある。

Table 1. Oceanog raphical conditions when the drift ice were collected.

Locality		Off Abashiri	Beach of Abashiri Bay	Off Hanasaki	Beach of Hanasaki Bay
Date (1949)		March. 23	March. 24	March. 27	March. 27
Air temp. °C		−1.2	3.2	0.5	1.9
Surface water temp. °C		−1.2	−0.7	0.4	1.6
Salinity of Sea water ‰		32.43	31.15	33.40	32.63
Conditions of drift ice	Hardness	H_2	?		
	Colour	white and opaque	equal	equal	equal
	Air bubble	porous with small air bubble.	equal	eqnal	equal
	Thickness	18.0cm	15～25 cm	——	30.0 cm
Cl. content in drift ice‰		0.903	0.193	1.830	2.762
Volume of sample (l)		8.5	10.0	6.0	7.5

本報告は函館海洋氣象台の大黒實技官と共に網走及根室沖の流氷を調査した際に採集した材料に就て述べんとするもので、此の機會を與えられた函館海洋氣象台竹内能忠台長並に採集に當り助力を得た大黒技官に感謝するものである。又流氷採取に種々便宜を與えられた日本冷藏會社網走出張所高橋

正三郎氏、網走測候所長二宮三郎氏、日魯漁業會社花咲出張所長太田一郎氏等に謝意を表する。

2 材料採取並に海況

觀察した材料は一昨年（1949）3月網走及び花咲根室町の兩地點で採集したもので流氷採取時の海況は第1表に示す。

流氷を採取した地點の海水中からもプランクトンを同時に採集した。流氷中のプランクトンは流氷を實驗室に持歸りストーブで融解し、この水をミューラガーゼ25番の小型ネットで濾過して採集した。流氷中に含有される塩素量は結氷狀況或は經過時間その他の條件で差が出來るが、第1表に示した通りで0.9～2.7%の範圍にあり、花咲のものはCl量は多かつたが、これは流氷が融解中のため多孔質となつて居り海水が僅かながらこの孔に浸入したゝめと考えられる。須田(1932)も根室沖流氷及沿岸結氷でも1.69‰を觀測し大體今回の結果と近かつたが、田村、杉浦（1948）の南氷洋の流氷中のCl量0.06～0.21‰に比べると遙かに多かつた。又 Rund（1930）が南氷洋の流氷中の鹽分を測定した場合もS=3.75‰であつた。

水溫は流氷の標流する海區は一般に低いが今回も網走港外では－1.0°C前後、又花咲港外では0°C前後であつた。

今年の根室及び網走に於ける沿岸結氷並に流氷の去來狀況は第2表の様であつた。即ち平年に比べて結氷、流氷共に遲れてゐる。

Table 2. The day of the appearance of drift ice and freezed at coast.

	Freezed at the coast		Difference from average year		Appearance of drift ice		Difference from average year	
Locality	Beginning	End	Beginning	End	Beginning	End	Begnning	End
Nemuro	Jan. 8	Apr. 10	8 days	10 days	March. 20	Apr. 20	40 days	19 days
Abashiri	Jan. 27	Apr. 15	10 〃	14 〃	Jan. 24	Apr. 23	9 〃	3 〃

3 結　　果

以上の4地點で海水中並に流氷中から夫々4標品合計8ケの標品に就て出現したプランクトンの種類を示せば第3表の通りである。

Table 3. The species of plankton appeared in sea water and drift ice.

Species \ Locality	off Abashiri		Beach of Abashiri		Off Hanasaki		Beach of Hanasaki	
	Sea water	Drift ice	Sea water	Drift ice	Sea water	Drift ice	Sea water	Drift ice
Phyto—plankton								
Arachnoidiscus ornatus				RR				RR
Asterionella kariana					C		C	
Auliscus caelatus						RR		
Berellochea malleus				RR				
Biddulphia aurita	+	R	CC	R	CC	RR	CC	+
B. pulshella				RR				
Chaetoceros atlanticum	+		+	RR	+		R	RR
Ch. a. var. neapolitana	+		+					
Ch. criophilum	C	+	C	RR	RR	RR	R	R
Ch. contortum	R							
Ch. debile							+	
Ch. decipiens	+		+		R		R	RR
Ch. diadema					+		+	

(Continued)

Species \ Locality	Off Abashiri		Beach of Abashiri		Off Hanasaki		Beach of Hanasaki	
	Sea water	Drift ice	Sea water	Drift ice	Sea water	Drift ice	Sea water	Drift ice
Ch. radicans	+		R				R	
Ch. teres					RR		R	RR
Corethron criophilum	RR		RR		+	R	RR	RR
Coscinodiscus asteromphalus	R		R		+	R	RR	RR
Cos. radiatus	R		RR	RR	R	RR	RR	RR
Cos. sp.				RR				
Fragilaria oceanica f. circularis	C		C		R		+	
Fragilaria sp.	CC	RR	CC	R	R	+	R	R
Lauderia borealis	+		R					
Leptocylindrus danicus	RR							
Licmophora Lyngbi			R	RR				RR
Melosira dubia?				RR				
M. sp.				RR				
Navicula spp.	+		C	RR	R	RR	R	R
Nitzschia seriata	R		RR					
Pleurosigma affine	R	C	R	R		C		RR
Rhabdonema arsuatum				RR				
Rhizosolenia alata					R		RR	RR
Rh. alata f. curvirostris	R		R					
Rh. hebetata f. semispina	R	RR	R	RR	R	RR	R	RR
Rh. h. f. hiemalis	R							
Rh. styliformis								RR
Stephanopyxis turris	+	R	+		RR		R	RR
Thalassiosira decipiens	CC		C		+		+	
Th' sira hyalina	CC	C	CC	CC	+	C	R	R
Thalassiothrix longisima	+		+		+	RR	+	RR
Th' rix nitzschioides	+		+		C	RR	+	R
Zoo-plankton								
Ceratium arcticum		RR						
C. candelabrum								RR
C. fusus			RR					
C. macroceros subsp. gallicum			RR					
Peridinium conicum		RR						
P. sp.	RR	RR					RR	
Favelle sp.		RR						
Parafavella gigantea	R	RR						RR
Ptychocylis obtusa	R		RR		RR		RR	
Tintinopsis angustior					RR			
T. japonica					R	RR	R	RR
T. urnula				RR				RR
Rotalia papillosa						RR		
Acartia clausi					R		RR	
Calanus plumchrus	RR		RR					
Eurytemora herdmanii			C		R		+	
Harpacticus uniremis			R					
Oithona similis	R		R		R			
Oncaea sp.			RR					
Paracalanus parvus					R			
Pseudocalanus elongatus					R			
Nauplius of copepod			R		R	R	R	R
Corophiidae (Amphipoda)			R					
Nauplius of Baranus					RR			
Hydrachna sp.						RR		
Polyshaeta larva			R		RR		RR	RR
Sagitta hexaptera					RR		RR	
Total species	30	11	35	18	31	16	29	27

プランクトンの總數は67種でこの中珪藻類が最も多く46種を占め次で原生動物13種 (Tintinoinnea 6, Dinoflagellata 6, Foraminifera 1), 甲殻類11種 (Copepoda 9 その他) その他であつた。

海水中のプランクトンと流氷中のプランクトンを比較するに、一般に海水中ではプランクトンの種類は2倍近くなつて居り、その組成の狀態からも流氷中のプランクトンとは相違し兩者の間には明かに水系の異なることが指摘出來る。

海水中のプランクトンは4地點を比較するに大體網走、花咲の兩區は夫々異る出現狀態が認められるが又沖合と沿岸部でも僅か乍ら區別が出來る。

流氷中のプランクトンに就て比較するに4つの標本共に出現狀態が異なる結果が認められた。小久保博士 (1932～'36) が花咲 (根室) 沖の冬季間 (流氷期3月) のプランクトンに就ての觀察によれば第4表に示す通りである。出現種も今年の結果と大差なく大體同一海區では同時期に至れば例年似た樣なプランクトンの出現を見ることが分る。

Table 4. The plankton appeared at Hanasaki. (March)

Year	1931	1932	1933	1949
Species number of plankton	27	30	26	31
Diatom	26	28	26	20
Diroflagellata	1	1	0	0
Tintinnoinea	0	1	0	3
Copepoda	0	0	0	5

松平 (1932) は根室港の沿岸結氷中から8種、同所の流氷中から19種のプランクトンを見出して居り、流氷中には寒海種の多い點から寒海で結氷したものが漂流したものであると指摘している。

今回の觀察でも第3及5表に示された樣に各海區で流氷と海水中とでは出現したプランクトンの種類及び組成が違う。即ち第5表に見られる樣に海水中のものは流氷中よりも種類が多く又夫々特有の種類が含まれる。兩海區共に海水中では沖合も沿岸も殆んど出現種に變化はないが流氷中のプランクトンは各海區共又同一海區でも沖合と沿岸部のものとの間には著しい相違が認められた。

Table 5. The number of plankton species compared with drift ice and sea water.

Locality	Off Abashiri		Beach of Absahiri		Off Hanasaki		Beach of Hanasaki	
	Sea water	drift ice	Sea water	drift ice	Sea water	drift ice	Sea water	drift ice
Total species	30	11	35	18	31	16	29	27
Peculiar species in sea water	22	—	25	—	19	—	11	—
Peculiar species in drift ice	—	3	—	8	—	4	—	9
Common species	8	8	10	10	12	12	18	18

4 結　　論

流氷中には夫々特有のプランクトンの種類及び組成が見られるので異つた海區又は異つた季節に結氷したものと推定される。然し此の場合結氷期前のオコツク海のプランクトンの分布狀況が明かでないから流氷がどこから漂流して來たものかを斷定することは困難である。更に流氷を各海區で數回採取しこの中のプランクトンを觀察することにより漂流の經路とか、漂流速度をも推定出來る可能性もある。兎に角流氷の中には多くのプランクトンが埋藏されて居るので之が研究は興味のあることである。(研究費の一部は文部省科學研究費の補助によつた。こゝに厚く感謝する。)

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（水產科學研究所業績 第59號）

中層トロールに關する一考察

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A STUDY ON FISHING TRAWL OPERATED IN ANY DEPTH OF SEA-WATER.

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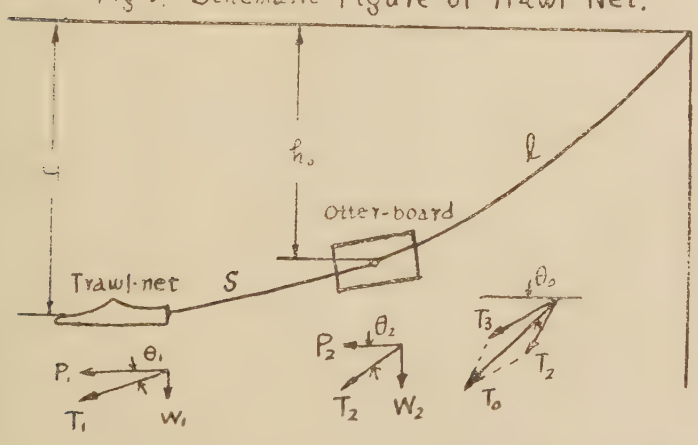
The authors have tried a study on the capability of fishing trawl operated in any depth of sea-water with type of ottertrawl.

If the values of the weight and resistance of trawl net and otter-board in water are given, the relation between the length of warp and the depth of water can be estimated, supposing that the form of the warp agrees with a catenary curve. (In Fig. 1)

The computed numerical values are shown in Table 1.

近時海中任意の深さに於ける魚類を捕獲するための中層曳網が考慮されている。例えば北海道に於ける鰊、鱈等の中層トロールや、魚類生態調査のための稚魚トロール等これである。海中任意の深さに網を保持しつゝ曳行するための機構[1]については種々考えられるが、曳網として最も普及された、オッタートロールの形式による中層トロールについて、二、三の假定のもとに、ワープ、網、オツターボード等にかゝる垂直面内の力の釣合から、ワープの長さと、水深との關係を求めた。こゝに、ワープ、網、オツターボードは同一垂直面内にはないが、上下方向の釣合についてのみ考える場合には、各々その面内の分力をとれば、二次元の問題として取扱つて差支えない。そこで第1圖に示す如く、船の位置を座標原點とする水平、垂直二軸をとり、符號を次の如く定める。

Fig 1. Schematic Figure of Trawl Net.



h_0 : Depth below the surface of the water till the otter-board. in m
H : Depth below the surface of the water till the trawl net. in m
l : Length of the warp. in m
S : Length of the hand rope. in m
$2W_1$: Trawl net weight in water. in kg

$2P_1$: Trawl net resistance in water. in kg

W_2 : Otter-board weight in water. in kg

P_2 : Otter-board resistance in water. in kg

θ_1 : Angle of the resultant T_1 to the horizontal line, where $\overline{T}_1=\overline{P}_1+\overline{W}_1$

θ_2 : Angle of the resultant T_2 to the horizontal line, where $\overline{T}_2=\overline{P}_2+\overline{W}_2$

θ_0 : Angle of the resultant T_0 to the horizontal line, where $\overline{T}_0=\overline{T}_1+\overline{T}_2$

ω : Warp weight per unit length in water. in kg/m

然る時は次式が成立つ。

$$\tan\theta_1=W_1/P_1 \cdots\cdots(1); \qquad \tan\theta_2=W_2/P_2 \cdots\cdots(2);$$

$$T_1=\sqrt{W_1^2+P_1^2} \cdots\cdots(3); \qquad T_2=\sqrt{W_2^2+P_2^2} \cdots\cdots(4);$$

手綱の水中重量が網の抵抗に比して大ならざる場合には、手綱はほゞ直線をなすから、網にかゝる力T_1は手綱を通して、そのまゝの方向でオツターボードにかゝる。從つてワープの下端に於て、T_1とT_2とが同時に加わることになり、次の式が成立つ

$$T_0=\sqrt{(P_1+P_2)^2+(W_1\pm W_2)^2} \cdots\cdots(5); \qquad \tan\theta_0=(W_1\pm W_2)/(P_1+P_2) \cdots\cdots(6);$$

（負號はオツターボードの浮力が大きく、水中重量が上向きの時である。）

次にワープの下端に於て上記の力T_0がθ_0の方向に加はる時のワープの長さと、ワープ下端の水深との關係を求める。

ワープが流れの方向となす角が小なる時は、ワープにかゝる抵抗[2]は、その水中重量と、張力とに比して小とみなされるので、これを無視すれば、ワープの任意の線素について、次の式が成立つ[3]。

$$dT/dl=\omega\sin\theta \cdots\cdots(7); \qquad T/\zeta=\omega\cos\theta \cdots\cdots(8);$$

$$\zeta\, d\theta=dl \cdots\cdots(9); \qquad dh=dl\sin\theta \cdots\cdots(10);$$

但 ζ は線素の曲率半徑である。

(10)を(7)に入れて

$$dT=\omega\, dh; \qquad \text{故に } T=\omega h+C$$

$h=-h_0$で$T=T_0$なる故 $\qquad T=T_0+\omega h+\omega h_0$

更に$h=0$で$T=T'$とすれば、ワープの上端に於ては$T'=T_0+\omega h_0$ ……(11)

次に(9)を(8)に入れて

$$T\, d\theta=\omega\cos\theta\, dl$$

これと(7)とより dl を消去して

$$dT/T=\tan\theta\, d\theta; \qquad \text{故に } \log T=-\log\cos\theta+C$$

こゝに $\theta=\theta_0$で$T=T_0$ $\qquad$ 故に $T\cos\theta=T_0\cos\theta_0$ ……(12)

(7)と(12)とより

$$dl=\frac{dT}{\omega\sin\theta}=\frac{dT}{\omega\sqrt{1-\cos^2\theta}}=\frac{dT}{\omega\sqrt{1-\left(\frac{T_0}{T}\cos\theta_0\right)^2}}$$

故に $l=\frac{1}{\omega}\int_{T_0}^{T_0+\omega h_0}\frac{dT}{\sqrt{1-\left(\frac{T_0}{T}\cos\theta_0\right)^2}}=\frac{T_0}{w}\left(\sqrt{\sin^2\theta_0+2\frac{\omega h_0}{T_0}+\left(\frac{\omega h_0}{T_0}\right)^2}-\sin\theta_0\right)$ ……(13)

更に兩邊を h_0 で割れば

$$l/h_0=\frac{T_0}{\omega h_0}\left(\sqrt{\sin^2\theta+2\frac{\omega h_0}{T_0}+\left(\frac{\omega h_0}{T_0}\right)^2}-\sin\theta_0\right) \cdots\cdots(14)$$

θ_0に種々な角度を與えた時、$\omega h_0/T_0$とl/h_0との關係について數値計算すると、第1表の如くなる。

尙 h_0 が與えられると網の位置は次式から容易に求められる。

$$H = h_0 + S \sin \theta_1 \quad \cdots\cdots (15)$$

Table 1. Relations between l/h_0 and $\omega h_0 / T_0$ when θ_0 is a parameter.

$\omega h_0 / T_0$ \ θ_0	l/h_0 0°	5°	10°	15°	20°	25°	30°	35°	40°
1/2000	63.24	11.13	5.66	3.84	2.91	2.39	1.99	1.74	1.56
1/1000	44.73	10.81	5.64	3.82	2.91	2.38	1.99	1.74	1.55
1/500	31.64	10.27	5.59	3.81	2.90	2.36	1.99	1.74	1.55
1/200	20.04	9.12	5.44	3.68	2.89	2.34	1.99	1.73	1.55
1/100	14.17	7.96	5.05	3.66	2.86	2.31	1.97	1.73	1.54
1/80	12.64	7.51	4.92	3.57	2.80	2.30	1.96	1.72	1.54
1/50	10.04	6.59	4.60	3.44	2.74	2.27	1.96	1.71	1.54
1/40	9.00	6.16	4.43	3.36	2.69	2.25	1.93	1.70	1.53
1/20	6.40	4.89	3.81	3.06	2.53	2.17	1.87	1.66	1.50
1/10	4.58	3.79	3 16	2.68	2.29	1.94	1.78	1.60	1.47
1	1.73	1.64	1.57	1.49	1.42	1.36	1.29	1.25	1.20

こゝに注意すべきことは、h_0 が小さくて（例えば 1 m）、表から求めた l の値も亦小さい場合（例えば 2.9m）には、オツターボードの開張が制限される。從つて l の値は、オツターボードの開口度によつて定まる最小値があるわけで、常にこれより大ならしめなければならない。もしこれより小なる時は、θ_0 を減少せしめるか、或は ω/T_0 を小さくして、l を長くする必要がある。

【附　記】

本報告は本學部井上教授主任擔當の科學試驗研究、噴火灣の總合的研究の一部をなす稚魚トロールの研究の豫備的考察としてなされたもので、同教授より終始指導を仰いだ。又本學部齋藤、川崎兩教授からは、しばしば有益な助言を得た。こゝに厚く謝意を表す。

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（水產科學研究所業績　第60號）

集魚灯に關する研究

第1報　二三の知見

三浦鐵雄（漁業第二教室）

STUDIES ON THE FISH ALLURING-LIGHTS.

1. SOME NOTES ON THE PRESENT STUDIES.

Tetsuo MIURA

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Fishing using fish alluring-lights has been much in operation in various fishing grounds of southern Japan, but it is not so much the case in Hokkaido. It was only since the end of the World War II that the skipper fishing by lift-net supported by poles using the above mentioned lights was introduced to the fishing in Hokkaido by the fishermen of Sanriku district, and there are very few studies concerning this method in Hokkaido, though there are several investigations about this in Honshu. In view of the fact that the conditions of the sea, habits of fish and methods of fishing in Hokkaido are generally different from those in Honshu, it is desirable carrying on the research in the field of Hokkaido, so as to make it more effective. The present writer has accomplished, to a certain extent, the research in this line, and come to some different conclusions from those hitherto published by the researchers whose fields of experiments had been exclusively limited to Honshu.

The first problem in the study of light fishing is to consider, which is more effective, the lamp above the water or one under the water. For this purpose, the illumination range of each type was examined by measuring visible depth to the Secchi disk in the water lit by each light, and also investigated the reaction of some species of fish for each type. From the result thus obtained, some remarks were made taking full advantage of the characteristics of the each type in the fishing that utilizes one of these.

The second problem must consider the advantages and disadvantages which depend on the various lighting mechanisms. For this purpose the visual sensitivity of fish was supposed and the writer calculated the transmission coefficients of lights of various wave-lengths at various depths in sea water, quoting Sawyer's measurements of absorption coefficients at 1m. depth. The conclusion was that such light source should be employed that might emit most effectively the light of the range of wave-length thus determined. It was pointed out that, among various types of lights now in use, mercury lamps and fluorescent lamps are more efficient for the purpose than tungsten lamps.

The third step to be made is to decide on whether to devise such a way of using fish alluring-light as is most adapted for the fishing method now existing or to invent such a new

method of fishing as is mostly adapted for the employment of fish alluring-light. Some remarks were made on this point.

1 緒　　言

集魚灯漁法は本州各地で盛んに行われているが、北海道は色々の原因から普及が遅れていた。ところが終戦後集魚灯利用サンマ棒受網漁法が本州より移入され、指導當局の奨勵もあつて、集魚灯を本道の各種漁法に利用せんとする積極的試みが行われるようになつてきた。しかし從來集漁灯に關する試驗研究は本州の漁場におけるものばかりで本道の漁場におけるものは殆んどなかつた。それで本州の報告を其儘信用して單に模倣する場合が多かつたので、大部分が期待に反する結果に終つている。本州の海洋條件、魚族の習性、漁法と、本道の夫とは一般に異なるので、本道には本道の漁場でなされた試驗研究が必要である。從來本道で集魚灯漁法が普及しなかつた原因として、第1に本道の海は一般に水溫差が激しく魚族適水溫帶が狹いので魚群密度が大であり、殊更灯を用いて集魚する必要がないとか、第2に比較的水溫が低く透明度も小さいので余程の大燭光を用いない限り集魚時間が延び集まる魚も少なくて效果がないとか、第3に本道では季節的洄游魚の漁獲を主とするが、海洋條件の相違もあつて魚脚が一般に速過ぎ灯に對する滯留時間が短くて操業が困難であるとか、色々のことがいわれていた。しかし根本原因は特に終戰前まで本州よりも比較的資源に惠まれた漁場をもち、又主として沿岸漁業に依存していた本道漁業者の保守性と研究の立遲れにあつたことは、本州漁業者の進出を契機とする現在の集魚灯利用サンマ棒受網漁業の普及がこれを立證している。これは又集漁灯不振の原因としてあげられる上述諸條件に對應する積極的研究の如何によつては必ずしも集魚灯が本道に不適であるとは斷定出來ない證據でもある。筆者は本道の漁場において二、三の魚類を對象に集魚灯の研究を續けてきたが、得られた結論が本州の漁場でなされた研究の報告と若干異なる場合もあり、又集魚灯に關する基礎的一般的事項についても二、三の知見を得たので、これらを報告し、今後の本道における集魚灯研究者の參考に供する。

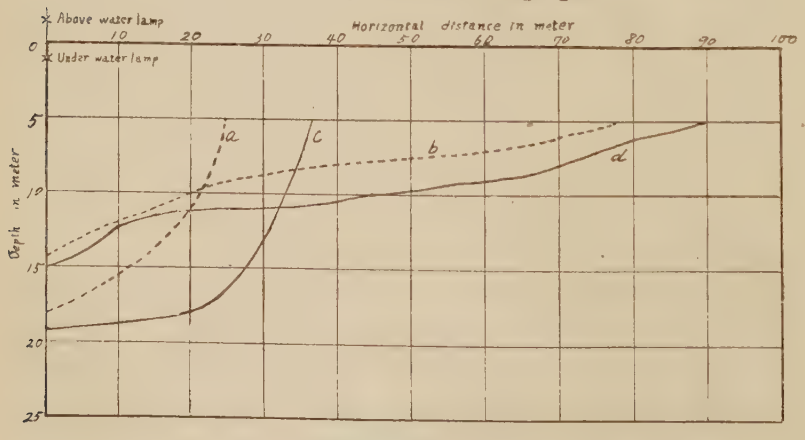
集魚灯の研究でよく問題になるのは、水上灯と水中灯との利害得失、光源の發光機構の種類による利害得失、集魚灯と漁法との組合せの問題等である。實際問題としてはその他設備費、耐久力、取扱いの難易等實用化のための問題もあるが、若し集魚成績良好のものがあればこれらについては追々と工夫改善して行くべきであろう。次に以上のような問題について本道漁場の魚類を對象とした實例によつて考察する。

2　水上灯と水中灯との利害得失

今日集魚灯といえば普通に水中式のものを指しているが、その何れが有利であるかは對象とする魚類の習性、漁法、及び海況によるのであつて一概に決められない。水中灯を推す人々[1]は、灯が水上にあれば光の一部が海面で反射されるが水中にあれば光の全部が一應水中で利用されるから能率がよいと述べているが、L. F. Richardson によれば實際の海面における Albedo は 0.06 程度であり、この値から推定しても、他の利害得失と併せ考えれば左程水上灯が劣る理由にはならない。水中灯の場合、一般に魚は光源を遠捲きにして游泳し、時たま光源近くに來るものがあつても瞬間反轉逸脫する。水中灯を推す人々は、これを魚は自身の好む照明のところに集まるとか、明暗の境に集まるとか說明するが、これは次の實驗の結果と矛盾する。サンマ棒受網漁業船の網側集魚灯（筆者が利用したの

は100V, 500W, 電球10個を一組にして大きな反對笠の中に納めた水上灯、第4，5，6，圖）で海面上方約2m の位置より照射すると、サンマは光源直下の海面下約2m のところを中心にして密集し、相當長時間照射しても所謂魚落しない。然るに水中灯の場合には100V, 60W, 電球1個でも光源を遠捲きにして游泳し、灯具のちよつたとし揺れにも敏感で散り易く短時間で魚落する。兩者についてサンマ游泳圈の照度を比較すれば前者の方がはるかに大きく、結局サンマに適度の照明は、水中灯によるその游泳圈の照度より大きい。純理的に考えれば生物の光に對する感覺は光化學反應の結果であるから、全刺戟値をCとし、光の單位時間の刺戟値をI、刺戟時間をtとすれば、Bunsen-Roscoe の法則、C=It. 又は之を一般にした Shwarzchild の法則、C=Itp（p：生物によつて決まつた常數）が成立する。水中灯に對するサンマの游泳圈は、サンマに對するCが最適なる區域であると說明出來る。ところが上述の比較實驗における水上灯の場合は水中灯の時よりもIもtも大きいからCの値が增しこれをサンマ自身の最適値にするために水中灯の時の游泳圈より大きな徑の游泳圈を理論上つくらねばならぬ筈である。然るに事實は全く逆である。即ち刺戟光源がサンマの棲息する水中にあるか外にあるかによつてサンマに對する最適刺戟値が異なることになる。又サンマは灯が水面の上にあるか下にあるかに關係なく、等しいI，tの値に對しても、群密度の小なる時は散り易く大なる時は散り難い。即ち群密度の如何によつても最適刺戟値が異なる。即ちサンマに對する最適刺戟値 Cはサンマ自身の置かれた環境によつて異なつてくる。一般に他の生物の場合にも、その生物に對する最適刺戟値Cは生物の種類とそれが置かれた環境とによつて定まり、生物に對するCの値を一義的にI，t，の測定から出しても[2]凡ての場合に適用出來ぬと考えられる。若しCの値の變化によつて一般に魚類の游泳圈の大いさを說明するのであれば、各魚類の置かれた環境に屬し、しかも彼等が感知するI，t以外の凡ゆる刺戟源の刺戟値の代數和たるCの値をとるか、さもなければ環境の說明がなされなければならぬ。サンマ棒受網漁法には上述のような灯に對するサンマの反應から考えて本道では水上灯の方が優れている。又本道イカ釣漁船に水中灯を使用すると、イカは深層に誘集されトンボ釣は良好になる。時たま光源近くに浮上してくるものがあるが瞬間光源のために目つぶしでも喰つたように墨を吹いて逸脫する。前記法則の最適刺戟値がイカについては非常に小さいわけであるが、深層に集まつた頃合をみて光の强さを減じて暗くすれば浮上して來そうであるが明暗の變化に非常に敏感で直ぐ四散してしまう 結局本道のイカ釣漁業において漁獲の大勢を決するとされるハネグ釣が不能となり、現行漁法を變革せね限り水中灯は不適である。次に集

Fig. 1. Visible depth to the Secchi disk in sea water off Moheji near Hakodate lit by the fish alluring-lights.



a). Tungsten lamp (100V. 500W.) 1m. under water.
b). 〃 〃 〃 〃 1.5m. above water.
c). Mercury lamp (100V. 500W.) 1m. under water.
d). 〃 〃 〃 〃 1.5m. above water.

魚灯の要件として照明範囲の廣いものが望ましい。從來發光機構の異なる光源の水上及び水中における照明狀態を比較したものはあるが、[3][4] 同じ光源の水上及び水中におけるそれを比較したものはないようである。筆者が同一光源を水上及び水中にして透明度板の可視距離を測つて比較したところ、(第1圖)、水面方向には水上灯がはるかに廣く、水深方向には水中灯の方がやゝ大きかつた。しかし可視距離の測定には2割程度の誤差があるとされているので結局水深方向には兩者の間に大きな差はないと見てよい。水中の全照明空間を考えれば水上灯の方が廣くて有利である。しかし勿論水上、水中何れの灯を選ぶべきかは魚種、漁法も併せ考えて決定すべきである。例えば沿岸定置網に多數集魚灯を組み合せて漁獲する方法[5]でイカを漁獲するような場合はイカを浮上させる必要がなく又施設が他船航行の邪魔にならないようにするためにも水中灯でなければならぬことになる。

集魚灯による透明度板の可視距離測定は昭和24年12月24日、茂邊地沖合で行つた。調査船には日水所屬イカ釣漁船汐丸を借用し、測定方法は舷側より水中集魚灯を水面下1m に吊した時及水面の上方1.5m に吊した時の各々の場合について、共に曳航して來た傳馬船上より灯具の直下に透明度板を下し、函眼鏡によりその可視距離を測り、水平方向には傳馬船を移動し距離綱によつて5m 毎に測定した。光源として100V, 500W, の白熱灯及び水銀灯の2種を使つた。目下海中照度計を製作中であるから精密な比較は追つて發表する。

3　光源の發光機構の種類による利害得失

光源の發光機構の種類による測光特性とか、或は水面及び水中での性質とか、純光學的問題については研究し盡されているが、實際に集魚灯として使用する立場からこれらの光源を比較檢討した報告はあまりない。又或種魚類の視覺に關しては色々の角度から研究はされているが[7]、しかし例えば色覺の研究に魚類の視感度を考慮に入れた研究はあまりない。實際に集魚灯の光源として使用する立場から、必要なデータを諸文献より引用し筆者の測定値も使つて現在得られる二、三光源の利害得失を調べ、又一、二實際漁場で經驗した本道魚類の光反應に對する見解を述べる。

一般に魚に色覺がある以上感じ易い色を出す光源が集魚灯光源として有利であろう。ところでサンマ棒受網漁業において、サンマは赤色電球の下では行動が緩慢となり漁獲に最適の狀態となるから、網側集魚灯は赤色電球にするか、又は白色電球と赤色電球とを混用すればよいとの意見があり[8]、又實際赤色電球を用いて火事場のような照明下で揚網している業者がある。いかにもサンマは赤色灯を好むように見える。しかし筆者の實驗によれば網側集魚灯も白色電球で一向差支えなく、サンマが網側集魚灯に移つてから點滅裝置(第4圖)により減灯して暗くしさへすれば赤色灯下の狀態と全く同樣になる。結局サンマは明るければ行動が敏感に、暗ければ緩慢になるのであつて、この場合サンマの行動を色彩の刺戟による反應と考えるよりも明暗の刺戟による反應と考えた方が妥當のように思われる。減灯の際サンマは一瞬驚ぐが、一旦灯についたサンマは直ぐ馴れて殘灯直下に密集するから、電力節約の見地からいつても點滅裝置を設備しておき揚網の時に減灯した方がよい。

元來色彩の刺戟と明暗の刺戟は混同され易く、魚の好む色を調べるには、その魚に對する各波長の光の同一視感エネルギーについて比較しなければならない。しかし夫々の魚類について視感度を知ることは不可能であり大體を推定して比較するより仕樣がない。假令輻射エネルギーが等しくても、その波長の如何によつては明暗の刺戟が異なり、人類の場合には555mμ. の光を最も明るく感じ、波長がそれから離れるに從つて減ずる。ところで一般に魚類の可視範圍は人類のそれと大差なく波長の短い部分はむしろ人類以上に感ずることが知られている。(人類：397—723mμ. 魚類：340—700mμ.)

これから推察して魚類の極大視感度を大體520mμ. としても大した的外れにはならないであろう。魚の好む色を調べるのは困難にしても、明るく感ずる光即ち520mμ. 附近の光を能率よく出す光源が集魚灯に有利であろう。次に各波長の光の海水中の透過の問題がある。集魚灯の要件として、水中を出来るだけ遠方に到達するような波長の光を能率よく出す光源が有利であろう。一般に海水は波長の短い光をよく透し波長の長い光を多く吸收する。海水による各波長の光の吸收率は、世界各地において實驗室に、現場に種々測定されているが[9]、現場における觀測は主として太陽の種々なる高度における鉛直方向の光の弱まる割合を水の厚い層に亘つて平均した消滅係數 (Extinction coefficient) であり、これらの値から生物學的に便利な、沿直に透入する或波長の光が水中の各層において何%位に弱まるかを知る透入率 (Transmission coefficient) を算出することは難しい。その點、實驗室の測定は水層1m の吸收率 (Absorption coefficient) であるが、比較的悉しく各波長毎に測定されており、透入率の算出が容易である。勿論水中の光の強さは海表面の狀態、水中浮游物の影響があり、實驗室内の結果をその儘現場の海水に當嵌める譯にはいかない。ところで未だ日本周海の水に對しては、上述のような現場の測定はあるが、實驗室の測定はあまり知られていない。筆者も本道海水の測定準備を始めたばかりで未だ發表の段階にない。それで今海水中における光の透入狀態の大體の傾向を知るために、Sawyer が Canad. Head Harbour 沖の Fundy Bay の海水を實驗室に持込んで測つた1m 水層の吸收率から透入率を算出し第2圖に示した。

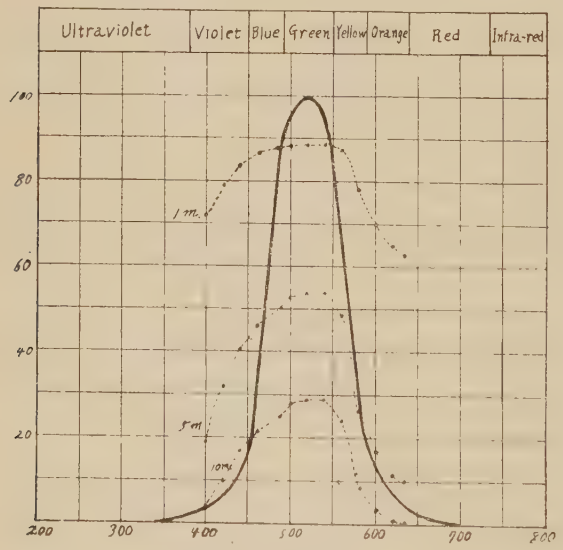


Fig. 2. Showing the transmission coefficients of light at various depths in sea water.—Dotted-lines. Supposed visual sensitivity of fi-h.— Full-line.

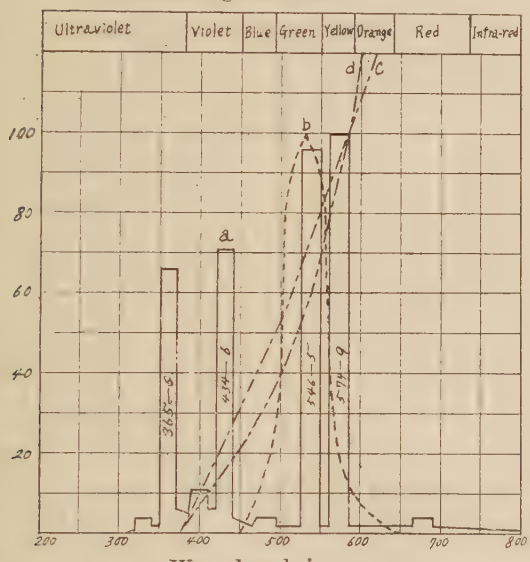
5,10m の曲線は Lambert の法則により 1m の曲線を5,10乘して求めたものに過ぎないが各波長の光の弱まる狀態の大體の樣子を見るために示した。この圖では540mμ. の光の透入率が最も大きい。Clarke[11] と James の Vineyard Saund, Whistle Bay, Buzzards Bay 等の海水の實驗室の測定値によると 570mμ. 附近の光の透入率が一番大きい。現場の海水においては一度散亂されて外に出た光が又散亂により逆戻りすることもあり、一般に實驗室の測定値から求めた透入率は現場の透入率より小さいのが普通であり、第2圖の透入率も現場海水で測ればまだ大きいかも知れぬが、各波長の光の透入率の相對位置は左程變らぬと考えてよい。圖は勿論本道海水の光の透入狀態を示すものではないが、世界各地の實測値のうち中庸的な例なので或程度參考にしてもよい。同圖に魚類の推定視感度曲線も示して見た。上述の各測定値の最大透入率と魚類の推定極大視感度を併せ考えて大體 520—570 mμ. の光を能率よく出す光源が集魚灯に有利なように考えられる。次に二三光源の 500—600 mμ. 間の發起能率を示した。(螢光ランプ、電球の計算値は文献[12]による)。

第2行の數字は電灯ノ消費電力(附屬器具の損失は含まず)のうちの何%が 500—600 mμ. 間の光になるかを示している。この表から水銀灯、螢光灯が白熱電灯よりも集魚灯光源として有利であろうと

Table 1. Reduced luminous efficiency emitted by various lights at 500--600mμ. wave-lengths.

Kinds of lamps.	Percentage of in-put.
100W. Mercury vapour lamp.	8.5
500W. 〃 〃 〃	8.8
15W. Greenish Fluorescent lamp.	9.8
〃 . Day-light coloured Fluorescent lamp.	4.4
100V.— 100W. Tungsten lamp.	2.2
〃 .— 500W. 〃 〃	2.2
〃 .—1000W. 〃 〃	3.1

Fig. 3. Showing the spectral energy curves of s veral light sources.



Wave length in mμ.

a: Mercury lamp (ca. 45 Lm/W)
b: Fluorescent lamp (ca. 50 Lm/W)
c: Gas-filled tungsten lamp (22 Lm/W)
d: Evacuated tungsten lamp (7.9 Lm/W)

考えられる。但し放電灯式のものには附屬器具の損失があるから上の數字から幾分割引しなければならぬが、それにしても白熱電灯のエネルギー極大値は赤外部にあり、集魚灯に有利な光が海中で僅小である。第3圖にこれら光源の分光エネルギー分布を示した。(白熱電灯は文献[13] 螢光灯は[12])

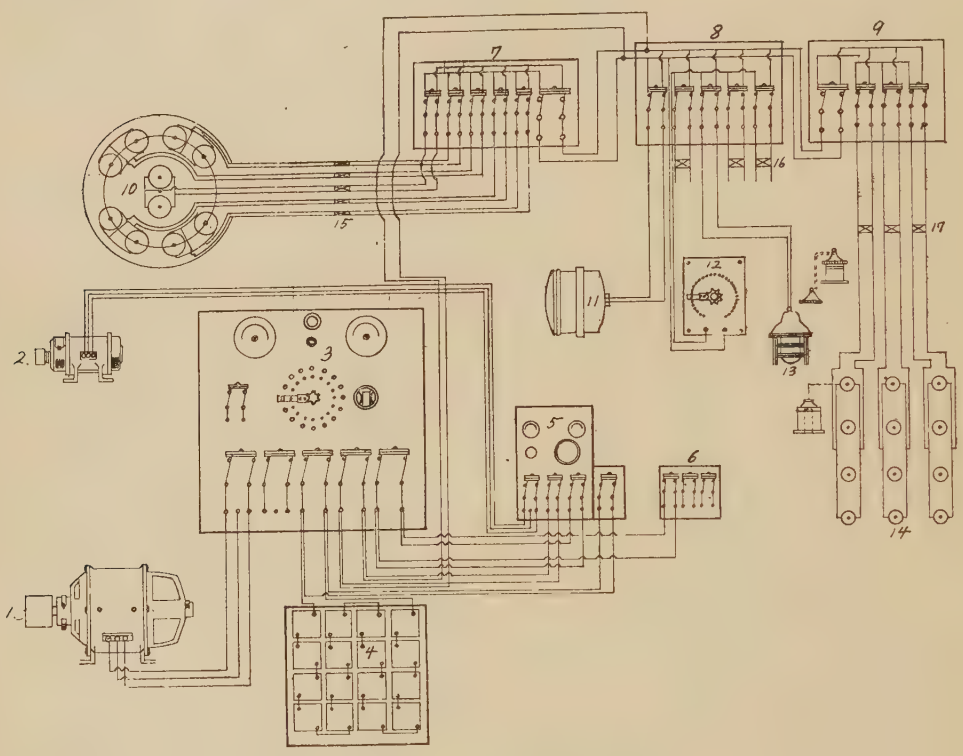
第 2, 3 圖を併せ考えると水銀灯、螢光灯が白熱電灯より有利であろうことが一層よくわかる。尙水銀灯の場合には 350—450mμ.のところにも大きなエネルギー分布があるが魚は波長の短い部分にもよく感ずるので上層では吸收されずに魚に感ずる。魚が光に感ずるのは光化學反應の結果である以上、化學作用の著しい紫外線を含むこの部分が魚にどんな作用を及ぼすかは今後の基礎的研究にまたねばならぬ。本研究第2報に水銀灯に對するスルメイカの反應を述べるが少く共イカに對してはこの部分が有害とは考えられず、むしろ集魚に有利のように觀察された。次に集魚灯光源としては一般には輝度の大なるものが有利であろうと考えられる。白熱電灯の場合は眞空で 100—300 sb. ガス入250—3,000 sb. であるが、G.S. 製 500W. 高壓水銀灯(第2報に詳述する)は 20,000 sb. で非常に大きい。螢光灯は輝度の點では甚しく劣るから輝度の刺戟に負の反應を示す魚種によい。集魚灯光源としては上述以外にも全光束、配光、發熱、光の動搖等の問題もあり、更に實用化の問題(取扱の難易、價格、壽命)もあるが、これらの問題に對しては白熱灯がその大部分を比較的有利に充しており、今直ぐ放電灯式集魚灯時代が來るとは思えぬが研究の進展により漸次放電灯式のものに切替えられるのではないかと考えられる。

4 その他の事項

集魚灯と漁法との組み合せの問題とは、現行の漁法をよりよく活かすような集魚灯の利用法を考えるか、逆に集魚灯の特性を活かした新漁法を發案するかということであるが、一二の經驗を述べる。現行イカ釣漁法を活かす限りは水上灯がよく、又サンマ棒受網漁業にも矢張り水上灯がよいことは前述した。ところでよく棒受網でイカが漁獲出來ぬものかと聞かれることがあるがその可能性はある。筆者はサンマ棒受網船に便乘し次のような經驗をした。先ず投網しておいてから、反網側集魚灯を點

灯するとイカは網側の船の蔭で暗くなつているところに誘集される。この時網の所在を覚らせないように撒餌をするなり、山手を引くなりして水面近く出来るだけ浮上させるようにして、機を見て迅速

Fig. 4. Showing the electric equipment of the N. S. K. fishing boat the Take-maru using lift net and fish alluring lamps.



1 : Dinamo used for the fish alluring lamps. — 7.5 K. W.
2 : Dinamo used for the lamps at workrooms. — 2.5 K. W.
3 : Main switchboard — 10 K. W., used for dinamo (1).
4 : Storage battery set. — AW 7 — 6; 16.
5 : Main switchboard. — 3 K. W., used for dinamo (2).
6 : Sub-switchboard used for the lamps at workrooms, equipped in the engine-room.
7 : Sub-switchboard used for the net-side lamps above waer, equipped in the steering room.
8 : Sub-switchboard used for the lamps under water, equipped in the steering room.
9 : Sub-switchboard used for the lamps above water, equipped in the steering room.
10 : Net-side lamps above water. One set is constituted of ten 100V.—500W. tungsten lamps. Each two lamps are able to be switched on and off at the same time.
11 : Search light. — 1 K. W. lamp used for searching for fish, equipped on the roof of steering room.
12 : Resistance-box : adjusting light-intensity of underwater lamps.
13 : Lamps under water; 4
14 : Anti-net-side lamps above water. Each four lamps are able to be switched on and off at the same time.
15, 16, 17 : Conc nt for vessel.

Fig. 5. Showing the arms supporting lamps equipped on the Take-maru. —40 tn. H. B.
Measured by Shaku. 1 Shaku ≒ 0.30 m

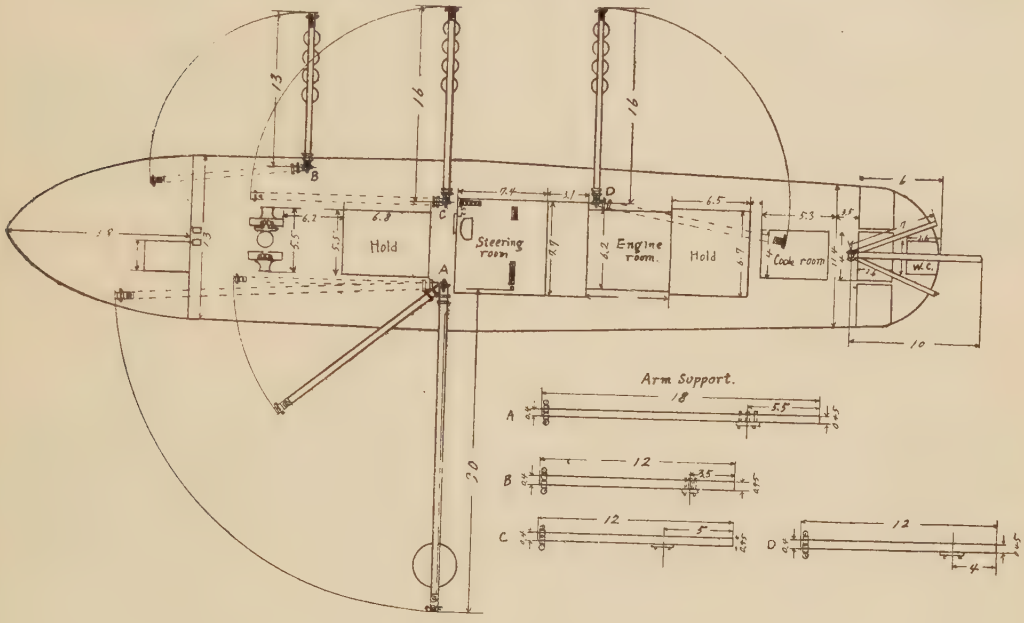
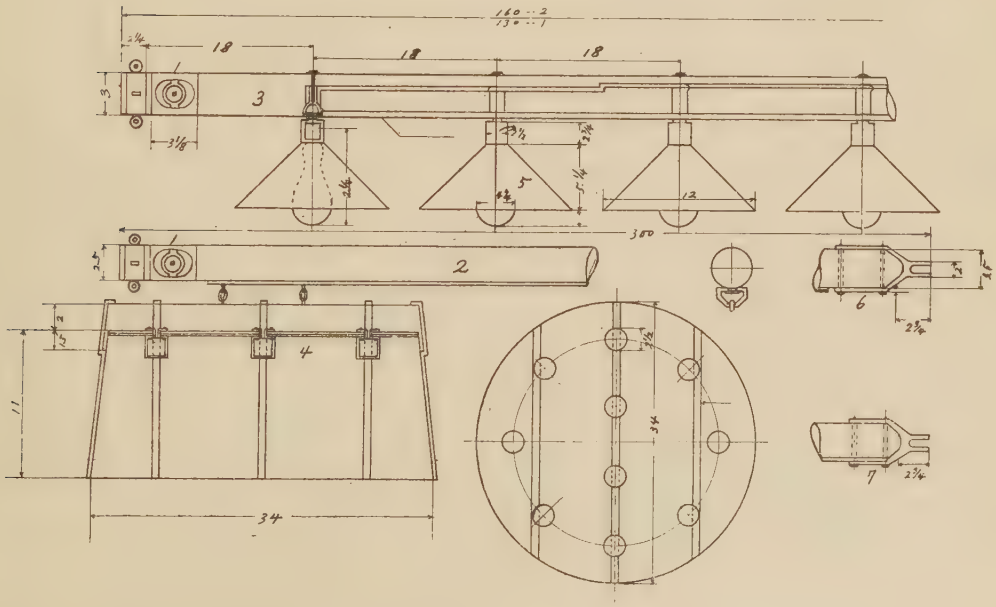


Fig. 6. Showing the detailed measure of lamp apparatus equipped on the Take-maru.
Measured by Sun. 1 Sun ≒ 0.03 m



1 : Roller which suspend the underwater lamps.
2 : Net-side lamp arm, made of cedar log
3 : Anti-net-side lamp arm, made of cedar log.
4 : Shade of net-side lamp.
5 : Shade of anti-net-side lamp.
6 : Goose-neck attached to arm.
7 : Goose-neck attached to arm support.

に沈子曳綱を引き上げると漁獲出來る。イカは敏感で前進後退が自由であるから網には側網を設け機械力で迅速に揚網出來るようにすれば尚よい。第4，5，6圖に試驗研究のため特に便利に設計された日本水產所屬竹丸の電機設備を示し參考に供する。

發電機を二つにしたのは在庫の一つを利用して計10K. W. にしたまでで特別の理由はない。水上灯の配置もこの方式が特によいという譯ではなく、最も効果ある配置を決める研究は今後の問題である。圖のような設備では船底はなるべく淺い船がよい。船底が3m位になると、サンマは網側に移るのが困難のようで船腹に衝突するものがある。以上スルメイカとサンマの例を主にして述べたが、その他筆者の經驗した本道產魚類で灯につくものをあげると、玉筋魚、片口鰮、鰤(30cm. 內外)、河豚等があるがこゝでは略する。

5 結　　言

本道漁場における魚類の反應を例にとつて若干の知見を述べたが、本文中に指摘した研究未完のものは今後逐次解決したいと考えている。終りに臨み本研究を後援された函館市役所、現場試驗に多大の便宜を與えられ熱心に支援された日本水產函館支社長原口安雄氏、同次長伊藤威雄氏、同事業課長岡田氏始め同課員の諸氏、特に直接協力された森田、村、淺野の諸氏、及び集魚灯用水銀灯の製作に當られて協力援助された日本電池の關係諸氏に深謝する。

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（水產科學研究所業績　第61號）

集魚灯に關する研究

第 2 報　水銀灯利用イカ釣漁業試験について

三　浦　　鐵　雄　（漁業第二教室）

STUDIES ON THE FISH ALLURING-LIGHTS.

2. ON THE EXPERIMENTS ON HOOK AND LINE SQUID FISHING USING THE FISH ALLURING MERCURY LAMP.

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The mercury lamp suggested in the previous report as much effective for the source of fish alluring-light was made available in squid fishing in the Tsugaru Straits, the result of which proved satisfactory, for the amount of catch thus effectuated was 1.41—3.22 times as much as in other cases adopted at present. The above data may vary according to the method of experiment.

The author pointed out that unless the equipment of the electric source is improved, the popularization of the fish alluring mercury lamp is hopeless.

1　緒　　言

北海道におけるスルメイカの生産は全國水揚高の半ば以上に達するが、その主産地は津輕海峽地方である。漁獲の大部分は釣漁によるものであるが、イカ釣船はその殆んどが 1—3K. W., 24 V. 直流發電機に蓄電池を併用し、18—24 V., 50—150 cp. の裸電球 1—2 個を船の中央部支柱に取付けて、作業兼集魚灯の役目をさせている。釣方は二法あり、深層のイカを釣り上げる方法をトンボ釣、浮上して來た時の釣方をハネグ釣というが、一夜の出漁中にハネク釣の出來る回數が多い程漁獲能率が擧がるので、出來るだけイカを表面に浮上させたい。この目的の一つに上述の裸電球が用いられている譯であるが、勿論集魚灯といえる程の物でもなく、又漁法そのものが根氣のいる筋肉勞働だけによるので、最も原始的な漁業として各方面から改善が要望されているものである。筆者は本研究の第 1 報において、集魚灯光源として水銀灯が有望なることを述べたが、これを本漁法に適用し、水銀灯に對するイカの反應を觀察して本漁法改善の可能性を檢討する目的で、本試驗を實施したのでその結果を報告する。

2　試　驗　方　法

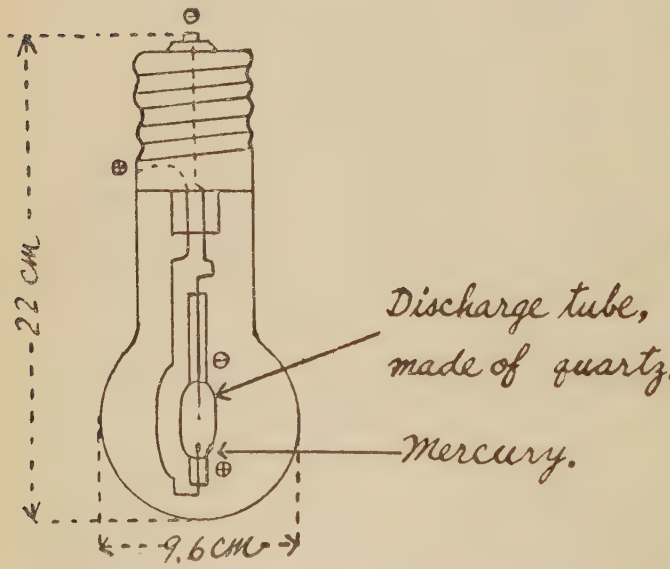
集魚灯の効果は、從來船（對照船）と集魚灯設備船（試驗船）との漁獲成績を比較して判定するこ

とにした。ところが漁獲量は灯の他にも多くの要因に左右され、灯のみによる變化だけを抽出することは實際問題として非常に困難である。即ち第1に對照船と試驗船との出漁の日、選んだ漁場、出漁日數が違えば當然變つてくるし、第2に船長の經驗、乘組員の數、腕前、努力の程度等によつても變つてくる。そこでこれら他の要因を出來るだけ除くために、對照船と試驗船は同じ日に、同じ漁場に、同じ日數だけ出漁して第1の要因による影響を除き、又試驗を二期に分けて前期では試驗船も從來通りの施設で出漁して兩船乘組員1人當りの平均漁獲量を求め、後期には試驗船に集魚灯を設備して同樣に平均漁獲量を求める。兩試驗において夫々對照船乘組員に對する試驗船乘組員の漁獲率を求めると、前期漁獲率で第2要因による影響の程度が判るので、これが後期にも左程變りがないものとし、後期漁獲率を前期漁獲率に比較することにより集魚灯の効果の程度が判る。試驗はこのような方法で行つた。又前報告に述べたように、スルメイカの習性と現行の漁法を活かすため水上灯とし、これを船の中央部の支柱に、船の蔭が舷側から2—3mまでの海面一帶に出來るような高さの位置に取り付けた。船の周圍に蔭をつくつたのは、明かる過ぎるとイカは行動が敏感で散り易く、又釣針が懸針なることを見破られ逃げられてしまうからである。

3 水銀集魚灯

使用した水銀灯は、集魚灯用として特に設計され、日本電池會社電機工場で製作された高壓水銀放電灯である。電球の構造を第1圖に示した。發光管は石英硝子で出來ており、球内には少量の水銀とアルゴン瓦斯が封入されている。起動裝置は第2圖の如き結線で、安定抵抗及び安定リアクトルは弧光を安定ならしめ、安定リアクトルは電磁石及び眞空開閉器と共に起動用高電壓を電灯に加えるためにも使用する。第3圖に眞空開閉器の構造を示した。電源電壓はD. C. 95—100V. である。回路を閉じると安定リアクトルの誘起電壓により電球に高電壓が加はり點灯するが暫くの間弧光が安定せず光度が低く電球電壓12—13V. で電流は約20A. 流れる。點灯後4—5分で水銀が完全に蒸發し弧光が安定して電球電壓は約70V. 電流は約7A. となつて安定狀態になる。測光特性及びエネルギー分布は前報告中に述べてあるから略する。

Fig. 1. Bulb of mercury lamp of high vapour pressure.



4 試驗期間

自昭和24年11月17日　　至同年12月19日

前期試験：11月17日—27日　　後期試験：11月30日—12月19日

Fig. 2. Connection diagram of starting apparatus.

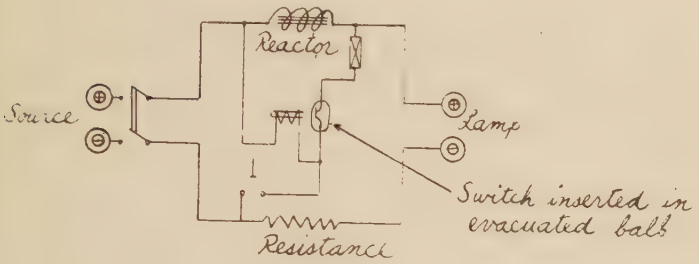
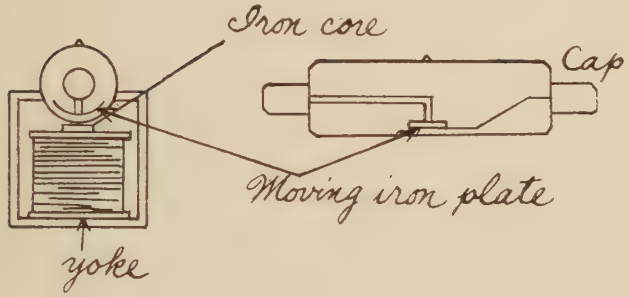


Fig. 3 Switch inserted in evacuated bulb.



5 試驗船

ウシオ丸（日水所屬，13.38tn. 40HP. H. B.）
乘組員10—18名

6 對照船

クキ丸（日水所屬，13.46tn. 42HP. H. B.）
乘組員10—19名

7 試驗海區

北海道渡島支廳管內惠山附近

8 使用電源

3K. W. 100V. 直流發電機にG. S. 製AR 7—6型蓄電池17個を併用

9 試驗成績

第1, 2表の通りである。

Table 1. Average amount of catch per capita compared with that made without mercury lamp.
Unit: kan (1kan=3.75kg)

Date	Amount of catch		Ratio
	Ship for Experiment	Ship for Comparing	
Nov.	kan	kan	
17	12	15	0.8
18	3	5	0.6
20	65	76	0.9
21	32	38	0.8
22	46	81	0.6
23	20	21	1.0
24	24	30	0.8
25	67	82	0.8
26	31	39	0.8
27	42	53	0.8

$\bar{x}_1 = 0.79$
$S_1 = 0.11$

Table 2. Average amount of catch per capita compared with that made with mercury lamp.

Date	Amount of catch		Ratio
	Ship for ExPeriment	Ship for Comqaring	
Nov.	kan	kan	
30	66	30	2.2
Dec.			
1	12	4	3.0
3	48	26	1.8
5	61	47	1.3
9	52	47	1.1
10	12	6	2.0
12	54	68	0.8
13	124	61	2.0
14	85	51	1.7
16	34	18	1.9
17	30	21	1.4
18	36	43	0.8
19	25	17	1.5

$\bar{x}_2 = 1.65$
$S_2 = 0.58$

10 經過について

荒天か故障等のため一方又は双方が休漁したり、試驗船が水銀灯取付けのため休漁して比較が出來なかつた日は漁期から除いてある。前期試驗で試驗船乘組員の對照船乘組員に對する漁獲率が小さいのは、對照船の根據地は海岸町にあり、同町には生え抜きのイカ釣本業者が多く、從つて對照船乘組員の腕前は確な者ばかりであるが、試驗船の根據地は仲濱町にあり、ここにはイカ釣本業者が少ないので前から成績が惡く一般に腕前が劣つているからである。1人平均の漁獲量を求めたのは、日により乘組員の數が變るので總漁獲量では比較出來ないからである。イカツケには歸港した時持ち上りといつて各自若干持ち歸つてしまうから眞の漁獲量は判らない。特に薄漁の時はこの影響が大きく試驗には困るのであるが、何んとも致方ない。試驗成績には兩船乘組員の持ち上りの程度を大體同じと見て考慮に入れていない。

11 試驗結果

前項に述べた假定の下で、漁獲率の變動は測定の誤差と考えられるので漁獲率の母集團は正規分布をなし、測定値はこれよりの任意標本と考えられる。現代統計學によれば、正規母集團 $N(m, \sigma^2)$ から大きさnの任意標本をとり、標本平均を $\bar{x}$, 標本分散を S^2 とすれば

$$t=\frac{(\bar{x}-m)\sqrt{n-1}}{S}$$

は、自由度 n−1 の t-分布 に從い、tの絶對値が λ より小さい確率が α になるような t の値を λ_α とすれば

$$\Pr\left\{|\bar{x}-m|<\lambda_\alpha\frac{S}{\sqrt{n-1}}\right\}=\alpha$$

即ち信賴度が α なる時の m の信賴區間は

$$\bar{x}-\lambda_\alpha\frac{S}{\sqrt{n-1}}<m<\bar{x}+\lambda_\alpha\frac{S}{\sqrt{n-1}}$$

となることが知られている。

前期試驗においては、$\bar{x}_1=0.79$, $S_1=0.11$、t-分布表によれば、自由度 10—1 の時 $\lambda_{0.99}=3.25$ 故に信賴度が 0.99 の時は

$$0.79-3.25\frac{0.11}{\sqrt{10-1}}<m_1<0.79+3.25\frac{0.11}{\sqrt{10-1}}$$

$$\therefore\quad 0.67<m_1<0.81 \quad\cdots\cdots(1)$$

後期試驗においては、$\bar{x}_2=1.65$, $S_2=0.58$. 上と同樣にして信賴度 0.99 の時

$$1.41<m_2<2.16 \quad\cdots\cdots(2)$$

(1), (2) より $\qquad 1.41<\frac{m_2}{m_1}<3.22$

故に 99% の確率で水銀灯により漁獲は 1.41～3.22 倍になつたものと推定される。但しこの効果は筆者の試驗方法よるものであつて、假令同じ水銀灯を用いても試驗方法が異なれば逆に負の効果を示すこともあり得る。

12 観 察 事 項

水銀灯による新漁法の可能性を見るために試験期以外の日に試験船を港内に出し、白熱電灯と水銀灯（どちらも100V. 500W.）とを交互に船側に持つてきて水面上方約2mの高さから海面を照射したところ、白熱電灯の時には集まつてきても直ぐ散つてしまうが、水銀灯の時には徐々散るのばかりでなく数匹が光源目指して跳躍し船内に飛び込んできた。このような事は、白熱電灯下ではないことで、水銀灯の出す光はイカに對し何か特殊の作用を及ぼすのではないかと考えられる。水銀灯の出す光には紫外線を含む350—450mμに大きなエネルギー分布があり（第1報所載）、これは水銀灯の特徴でもあるが、或はこの波長部分の作用によるものかも知れぬ。これについては、研究の上追つて報告したいと考えている。尚試験船乗組員は終漁日まで水銀灯の使用を喜んでいたが、これは水銀灯の効果を事實において示す有力な證據でもある。

以上の事實から水銀灯は現行イカ釣に有効であるばかりでなく、イカに對する新漁法を考える場合最も有望な光源であると考えられる。

13 結 言

津輕海峽地方のイカ釣に水銀灯が有効であり、又新漁法を發案する場合にも有利な光源であることを述べた。しかしこれを使用するには電源設備に100V.を要し、その上水銀ランプが高價であり附屬器具費も掛かるので急速な普及は望めない。現在の漁船の電源設備をそのまま轉用出來るように、24V.附近で點火する熱陰極を用いた低壓放電發光式のものが製作され、しかも實用化のための諸問題が適當に充されるならば普及するであろう。

終りに臨み本研究を後援された函館市役所、試驗に直接協力された日本水產會社函館支社及び日本電池會社の關係諸氏に深謝する。

14 文 献

統計科學研究會（1943）：統計數値表. 1. 河出書房

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STUDIES ON BOUND WATER IN THE FISH MEAT MUSCLE (I)

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I. INTRODUCTION

1. The definition of Bound Water.[1]

The problems of Bound Water have past time been studied from the standpoint of Biology and Physiology[2], and also will have many interesting points in future from the stand point of the applied field.

At first, Bound Water (or Living Water) was defined as that a part of the water in the living bodies bound with the muscle tissues. The other water which exists freely in muscle is called Free Water. This Bound Water has been considered as a factor for psychrotoleranty of living bodies, desictoleranty or maintaining lives of living bodies.

Lately it has been considered in colloidal chemistry and molecular theory that hydrophilic colloids such as protein or carbohydrates which are compositions of the body bind with Bound Water to form stable colloidal system, that is to form a protoplasm. In this case, the first reason for the binding of water with the tissue is as follows: the nitrogen-, oxygen- and hydrogen-atoms in the protein containing carboxyl-, hydroxylic-, imino- and amino-radicals combine with hydrogen- or oxygen-atoms of water and form hydrogen-binding. Therefore all proteins are considered to have Bound Water[3]. According to the studies of Weidinger and Pelser[1a] on gelatine, Bound Water is water which exists within the mycel of gelatine and Free Water is water which exists between the mycels.

Thus there are many definitions of Bound Water. In a word, the idea of Bound Water is different from the samples, the purposes of studies which investigators employ. But since bodily juice has always a close relation with protein[3c,4], therefore it is necessary that we have abundant studies in the problems of Bound Water, when we discuss the protein in fish muscles.

2. The methods of estimating Bound Water.

Methods of estimating the amount of Bound Water which have been used up to

the date are classified into three groups. But they agree that the amount of Bound Water is the difference between the total water content and the Free Water in the sample. The total content of water in the sample is calculated from the difference of the initial weight of the sample and the ultimate weight which is obtained by drying the sample for some time at 100°~110°C.

There are some different methods of estimating the amount of Free Water according to various ideas concerning Bound Water. One of the methods is the estimation of the frozen water contents from the assumption that Free Water will be frozen and Bound Water will not be frozen even though the muscle is kept at some constant low temperature such as −20°C. And another is based on the assumption that Free Water behaves as a solvent, but Bound Water does not do so. And the rest is the chemical estimating method.

Those methods contained few other methods can be summarized as follows:

(1) Freezing methods: (a) Calorimetric method[5]; A sample which was frozen at −20°C is put into the Calorimeter and Free Water is estimated from the latent heat of the melting of the frozen sample. (b) Dilatometric method[6]; The quantity of the ice (this is Free Water frozen) in the sample which was frozen at −20°C is estimated from the change of the volume of the ice by the Dilatometer. (c) Direct estimating method of the amount of water which is equivalent state to ice[7].

(2) Solvent methods: (a) Method concerning the depression of the freezing point[8]; This method is suitable when the sample is liquid. Free Water is estimated from the depression of the freezing point in Centigrade degrees; when 0.01 M of saccharose is dissolved in 10 gm of test solution, if the test solution is Free Water only, a normal depression of the freezing point will be noted, but if there is some Bound Water in the sample, the depression of freezing point will be correspondingly lower for the concentrated solution. (b) Method concerning the depression of the vapour tension[9]; This method is the same in the principle as the method concerning the depression of freezing point.

(3) Vapour tension method[10]: This method is determined from the equilibrium curve which show the relation between the amount of water contained in the sample and its vapour tension.

(4) Swelling tension method[7b,11]: This method is determined from the equilibrium curve which show the relation between the amount of water contained in the sample and its swelling tension.

(5) Chemical methods: (a) Cobaltous chloride method[12]; A sample, which was added with cobaltous chloride powder or was steeped in the cobaltous chloride

solution and dyed to pink color is dried at the temperature of 25°~30°C, then the sample will turn from pinkish blue to pure blue. At the time of changing color, the amount of water in the sample is considered as that of Bound Water. (b) Copper sulphate method[13]; This method is determined by estimating the change of concentration of dilute copper sulphate solution into which a sample is steeped. (c) Alcohol method[1a]: This method is determined by estimating the change of the specific gravity of alcohol in which a sample is steeped.

(6) Method by studying of physical properties[14]; This method is determined by studying the coefficient of friction of the surface, adsorptions-ability of the surface and other properties concerning the state of the surface of a gel membrane which hydrates with water at various temperatures, and the amount of Bound Water is discussed.

Recently Higashi and his coinvestigators[1] have studied the degree of binding strength of water by the electric method. In studying the various aspects of Bound Water, the electric method will have some greater significance for the studies in Bound Water.

II. HISTORY OF STUDIES ON BOUND WATER

1. Studies on Hydrophilic colloids and Meat muscle.

Studies on Bound Water were at first done about the state of water frozen in various substance. But recently the water in hydrophilic colloids and meat muscle has rather been studied from the standpoint of physical chemistry or physiology than from pure quantitative analysis.

Thoenes[5b] has studied the meat muscle tissues of dogs and other animals and said that 20~30% of water in their tissues is not frozen and this unfrozen water is Bound Water. He has also observed that in childhood of animals there are larger amount of Bound Water in their tissues, but in old age Bound Water decreases. Hardy[15] has demonstrated the existence of unfrozen water in gelatine which was frozen.

Moran[7b,16] has observed that when myogen and egg-albumin are frozen at −20°C, so 0.48 gm and 0.31~0.38 gm of water in these samples respectively per gm of dried matter remained unfrozen. He also has observed that when a disk of gelatine gel is frozen very slowly, such as at −20°C, water which exists in the neibourhood of the surface of the disk of gelatine gel is frozen and there remains 0.53 gm of water unfrozen per gm of dried gelatine in the disk. He has also observed that when the

muscle of cattle and of frogs are cooled gradually from 0°C, the amount of the unfrozen water becomes constant at about −40°C, that is to say, 0.43 gm of water per gm of cattle meat muscle and 0.45 gm of water per gm of frog meat muscle remains unfrozen, and he considered that these unfrozen water are Bound Water. Briggs[10c] has observed from vapour tension measurement of the gelatine gel that each gm of gelatine remains 0.33 gm of unfrozen water at −20°C. Kinoshita[17] has also observed the existence of unfrozen water in gelatine which was frozen. Kistler[15] examined qualitatively the existence of unfrozen water from the degree of condensation of frost that was formed from the fog in the tube which was cooled by dry ice and he has obtained the following result that a certain quantity of water remained unfrozen at even low temperature of −72°C. From the physiological and biological standpoints, Plank[19] has advocated so-called freezing phase. He has devided into four phases the freezing process of living things from −1° to −60°C, and he has pointed out the existence of biochemical Bound Water and colloidal Bound Water. But after that there is no reexamination about this problem.

There are many studies on the hydrophilic colloid of vegetable juice from old time, but the literatures on these studies are omitted.[8a,20]

Heiss[21] has said that the change of animal protoplasm during the refrigeration of animal kingdom foods are due to the variation of the volume of Free Water and the dehydration of the colloidal Bound Water in them, and he observed that two factors influencing these changes are the velocity of freezing and the pressure on cells, those factors are concerned with the temperature for freezing, various sizes of ice crystals in muscle, density of substance and thermal conductivity in muscles. Recently Joslyn[22] has discussed the relation between Bound Water and irreversibility in the change of colloidal properties during the freezing of foods.

According to the results of studies of each above mentioned investigators, in the case of refrigeration of colloidal matters or meat muscle, the possibility of the existence of Bound Water which is independently isolated from Free Water has been practically shown. And we know that in the case of refrigeration of foods Bound Water has important properties.

2. Bouud Water contained in the meat muscle of marine animals.

There are a few studies on Bound Water in meat muscle of marine animals. Higuchi[23] has studied the variation of the amount of Bound Water of the squid and flatfish meat in the course of drying at room temperature using the method of the depression of the freezing point and the calorimetric method. According to

his results, the amount of Bound Water is 3 to 5 % of the initial weight of the fish meat muscle, but it gradually increases during the drying, and when the ratio of the drying, ($^{W}/_{W_0}$), reaches 0.30, the amount of Bount Water of the fish muscle becomes from 6 to 10 % of the weight of the dried fish muscle and it has a tendency to increase in proportion to the degree of drying. Here W_0 is the initial weight of the sample, and W is the weight after drying. Kawakami[24] has considered that if the same amount of water in fish meat muscle as the amount of water in fish meat muscle that is frozen to ice is evaporated by drying, the depression of freezing points of both remaining solution should be the same, and he studied the relation between the depression of the freezing point and the variation of the weight of fish meat muscles in the course of drying by using carp meat muscle and observed that his results was exactly equal to Finn's result[25] which shows the relation between the freezing point and the amount of frozen water. From this point of view it will be assumed the existence of Bound Water in the carp meat muscle.

As stated above the probelms on Bound Water in the meat muscle are discussed from various ideas of estimating it from the standpoints of biological, physiological and colloidal chemistry and molecular theory. And in applied field there had been many studies on this Bound Water, but we have not yet remarkable results contrary to our expection[26].

The writer has wished to study various properties of Bound Water in the fish meat and to know the relation between Bound Water and protein of fish meat, taste of fish meat, and the growth of micro-organisms, etc. and wished to apply these results to the manufacture or processing of marine products.

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Ⅲ. STUDIES ON ESTIMATING METHODS OF BOUND WATER

1. Examination of the comparison between the methods of cobaltous chloride with vapour tension method and with the method by electric resistance.

As stated above, there are many methods for estimating the amount of Bound Water. But some of them have different ideas as to the principle of the estimating method. Owing to the upper mentioned difference of the ideas, the difference of freezing temperature of the water in the sample or the kind of added matters in the solvent method, from even the same sample we can not always obtain the same result. The reason for the disagreement of the results was discussed from various standpoints. Among these discussions, according to Briggs' theory[10b,c], the amount of water contained in the sample controls the activity coefficient of water (the water-activity) "a" at the existing amount of the water.

The water-activity of the sample, "a", is calculated by dividing the vapour tension of the water in the sample p_x by the vapour tension of the pure water at

the same temperature p_o, and these results are illustrated by a curve of the relative vapour tension p_x/p_o ($a = p_x/p_o$) and the weight of the amount of the water in the sample (the amount of water per gm of dried matter of the sample). This water-activity may be taken as a measuring rod defining the physical status of the water present in a system. When the water-activity is varied, it is an indication of a corresponding change in the free energy content of that water. That is to say, the less the water content of the sample becomes, the less the value of the water-activity, "a", becomes.

The water-content —water-activity curve which indicates the relation between the amount of water contained in the sample and the water-activity at the existing amount of the water, forms an identical continuous curve from the same sample even by various estimating methods. Because the various thermodynamic methods, for example even if vapour tension method, the method of the depression of the freezing point, Calorimetric method, Dilatometric method, Swelling tension methods, are only a means to obtain the water-activity in the sample.

As the estimating method of the amount of Bound Water, beside the above stated methods of thermodynamic methods, there are some methods by pure chemical operation, for example the cobaltous chloride methods by Hatschek or Oyagi. In these methods the sample can be handled at room temperature, and the operation is simple and convenient, so that these methods have been employed among investigators of Bound Water. But these methods have still some problems to be reexamined. Because in these methods also, they are suitable or unsuitable for some kinds of the samples, and there is an individual error, that is to say, the turning point at which a pure blue color from pink color of dyed sample in the course of the dehydration at temperature from 25°—30°C, is different according to the individual investigators.

The author has always employed this cobaltous chloride methods for estimating the amount of Bound Water in fish meat muscle. And he has found some suspicious point in these methods, then he has wished to try to reexamine various conditions. By the comparison of the results by the cobaltous chloride method with various other thermodynamic methods stated above, the author wished to make the significance of quantitative estimation of the amount of Bound Water in the sample clear.

The author will report here the results of the comparative examination of the states of water about the same sample by the cobaltous chloride methods, vapour tension method and the method by electric resistance.

(1) Experimental Methods.

(I) Sample

As sample the author has at first used the gelatine which has been employed for the study of Bound Water, and has compared the results from the gelatine with results of fresh fish meat muscle: Hatahata (Sandfish; *Arctoscopus japonicus STEINDACHNER*), Hokke (Atka Mackerel; *Pleurogrammus azous JORDAN et METZ*) and Yariika (A species of squid; *Loligo bleekeri KEFERSTEIN*). The samples of gelatine are one which is on the market (water content 13.04 %, ash 0.74 %) (The author calls it Sample No. 1) and one (water content 17.95 %, ash 0.69 %) (Sample No. 2) and the other which was purified by the Second Faculty of Engineering of Tokyo University (water content 18.66 %, ash 0.43 %) (Sample No. 3). These gelatines were supposed to be manufactured by acid treatment. The water solutions of these gelatines were pH 7.4.

(II) Cobaltous chloride methods.

The author has employed both the methods by Hatschek and Oyagi. Both these methods are the same in the principle of the estimating method. That is to say, the sample dyed with cobaltous chloride turns from a pink color to a pure blue color at one point in the course of the dehydration of the sample, and the amount of Bound Water will be known from the difference of the total content of water and the amount of Free Water which was estimated at the point of the change of color.

(A) Hatschek's method[12a]

Mix 10 gm of the sample of gelatine (as dried matter) and 5 gm of cobaltous chloride ($CoCl_2 \cdot 6H_2O$) and add an adequate amount of water to the mixture and dissolve it by heating. Pour the dissolved sample into a wooden cylindrical vessel (dia. about 3 cm, height about 0.7 cm), which is laid on a metal plate having a smooth surface.

After the cooling and solidifying of the gelatine, remove the cylindrical vessel from the metal plate, and dry gradually by standing it in the drier at 25°—30°C. Then the color of the cylindrically shaped gelatine turns gradually from pinkish red to violetish red and then to bluish violet from the outside of the cylinder of gelatine. After the color has turned homogeneously to pure blue, cut off cylindrically (dia. about 1 cm) the center part of dried blue colored gelatine. Put this cylindrical gelatine into a weighing bottle, and weigh the weight of bottle with the sample, W_1, and then dry it further in the drier at 100°—110°C until obtaining the constant weight, W_2.

In the case of estimation of the amount of Bound Water of fish meat muscle by using the Atka Mackerel meat, the author has employed the same method as above stated: Grind the fish meat, mix this fish meat with the definite quantity of cobaltous chloride The following procedures are the same as the gelatine. In the case of fish meat, the using of cylindrical vessel was experienced to be unsuitable, because the meat shrunken by drying falls off from the vessel.

The calculation by Hatschek's method shows the following :

(a) The amount of water in the blue colored sample (gm): $W_1 - W_2 = W$

(b) The weight of dried matter of the sample in the blue colored sample (gm): $G = W_2 \times \frac{g}{C+g}$ Here "g" is the weight of dried matter in the sample taken after the preparation of the sample. C is the weight of added cobaltous chloride without crystal water.

(c) The percentage of the amount of Bound Water in the dried matter of the sample: $\frac{100W}{W+G}$

(d) The amount of Bound Water per gm of the dried sample (gm):

$$\frac{W}{G} = \frac{W_1 - W_2}{W_2 \times \frac{g}{C+g}}$$

(e) The amount of Bound Water per gm of the dried sample which was mixed with cobaltous chloride (gm): $\frac{W_1 - W_2}{W_2}$

(B) Oyagi's method[12c]

Cut the air dried gelatine or fresh fish meat in slices about 1 cm square, and dye to a pink color by steeping the slices in a 10% cobaltous chloride solution. After 24 hours, take out this sample and absorb the solution attached to the surface of the sample with a filter paper. Put this sample into a weighing bottle or on a watch glass which has been previously dried and then weighed, and the initial weight of the meat is obtained as W_0. Then let this sample alone in the oven from 25° to 30°C, and dry until it turns to pinkish blue from pink color and then to pure blue. At the time of changing to pure blue color the sample must be weighed rapidly. The weight at this changing point of the color is obtained as W_1. Then dry further this sample for several hours in the oven of 100° to 110°C and obtain the constant value of the weight of the sample, W_2, according to the usual method. The calculation is shown as follows :

(a) Percentage of the total amount of water in the dyed sample: $\frac{W_0 - W_2}{W_0} \times 100$

(b) Percentage of the amount of Free Water in the dyed sample: $\frac{W_0 - W_1}{W_0} \times 100$

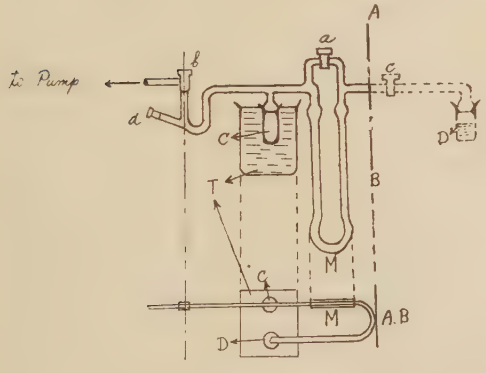
(c) Percentage of the amount of Bound Water in the dyed sample: $\frac{W_1 - W_2}{W_0} \times 100$

(d) The amount of Bound Water per gm of the dried matter containing cobaltous chloride without crystal water : $\frac{W_1 - W_2}{W_2}$

In Oyagi's method, the weight of the dried matter (without cobaltous chloride) of the dyed sample is not calculated. So the author shows the amount (gm) of Bound Water per gm of the dried matter containing cobaltous chloride as the weight of the amount of Bound Water per gm of the sample. The author has calculated the weight of the anhydride of cobaltous chloride which penetrated into the sample when the sample was steeped in 10% cobaltous chloride solution from the increasing difference between the weight of the dried matter of the original sample and the weight of the dried matter of the sample which was dyed in cobaltous chloride solution. The author has thus obtained the weight (gm) of Bound Water per gm of the dried sample, and compared the results by Hatschek's method with Oyagi's method.

(Ⅲ) Vapour tension method.

Fig 1. A Estimating apparatus of Vapour tens



The main part of the apparatus used for the vapour tension method consists of oil-manometer (M), sample bottle (C), distilled water bottle (D) which runs parallel with (C) by bending the glass tube attached to (D) from the A-B line and exhaust cocks (a), (b), (c), (d) (See Fig. 1). Bottles (C) and (D) are submerged in the same thermostatic vessel (T). Put 5~10 gm of the sample (in the case of the sample of gelatine, gelatine gel containing 80% of water is ground and added into (C)-bottle.) After (C)-bottle is attached to the apparatus, open (a)-cock and (c)-cock, close (b)-cock and (d)-cock, drive the air pump (guaranteed vacuum 0.1 mm Hg), then open (b)-cock slowly. After air in the apparatus is exhausted for about 5 minutes, close (b)-cock and (a)-cock at the same time. Read the equilibrium pressure between the vapour tension p_0, of pure water in the (D)-bottle on the scale of the manometer (M). After the estimation of the equilibrium pressure, open (a)-cock slowly, then open (b)-cock and let air fill the apparatus. Take out the (C)-bottle from the apparatus and wipe grease attached to the mouth of the bottle with absorbent cotton moistened with toluene, and then put another cap on the mouth of the bottle and weigh the weight of the bottle with the sample,

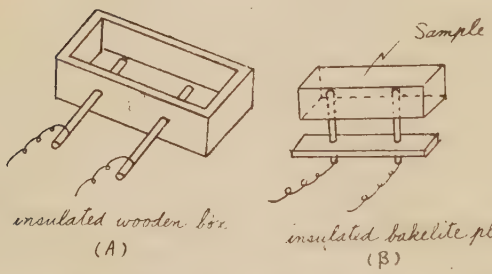
W_1. By repeating this treatment, after some time of exhausting of air from the apparatus, estimate the equilibrium pressures of p_2, p_3, p_4----p_n and weight of samples, W_2, W_3. W_4----W_n, at the pressures of p_2, p_3, p_4----p_n respectively. At last, after drying of (C)-bottle containing the sample, weigh the dried matter of the sample, W_a. From these results the weight of the total amount of water in the sample at each estimating time is calculated.

For the correction from the pressure by oil manometer to the pressure by Hg manometer, the formula $p_x = p_o - 0.0714 p_y$ is ascertained within the range of the temperatures between 5° and 16°C. Here p_x is the vapour tension of the water in the sample (Hg. cm) at the estimating temperature t°C; p_o is the vapour tension of pure water (Hg. cm) at the same temperature; p_y is the pressure read (cm) on the scale of the oil manometer.

(Ⅳ) The method by electric resistance (50 cycles resistance).

For the estimating of electric resistance of gelatine, the sample of gelatine containing various amounts of water, is dissolved and then these sol are poured into an insulated wooden box (A) (4.4×1.5×1.0 cm). (See Fig. 2, A).

Fig 2. Insulated wooden box and bakelite plate for the estimation of electric resistance.



Two copper poles are thrust through one outside wall of the box, and then cooled and solidified. (The length of the pole thrust into the sample is 0.7 cm, the diameter of the poles is 2.3 cm). Then this apparatus containing the sample is placed in a desiccator of 15°—16°C in which electric wire is arranged, and the electric resistance was made by Fuji Radio Co. and its cycle was 50, and its type was Wheatstone's bridge.

In the case of the estimation of the electric resistance of fresh fish meat, two copper poles which are fixed to the insulated bakelite plate are thrust through the fish meat filet (4×2×2 cm). (See Fig. 2, B). The distance between the two poles is 1.5—3.0 cm. The length of the pole thrust the sample is 0.7 cm and the diameter of the pole is 0.75 mm. In the case of the dried fish meat, the temperature of drying of fish meat is 20°—30°C, and then the sample which was thrust through by the pole is placed in the desiccator at 15°—16°C for some time before estimation of the electric resistance.

(2) Experimental results on gelatine.

(1) Results from the estimation of the amount of Bound Water in the gelatine by cobaltous chloride method were compared with the results from the vapour tension method and method by electric resistance.

Table 1 (Fig. 3) shows the variation of the amount of Bound Water in the sample No. 2 of gelatine estimated by the cobaltous chloride methods (Hatschek's and Oyagi's methods) at intervals of 30 minutes.

Table 1. Experimental course which show the variation of the amount of Bound Water at intervals of 30 minutes in the drying of the sample No. 2 of gelatine by the Cobaltous chloride Methods. (Hatschek's and Oyagi's Methods)

Drying time in hours.	Hatschek's Method				Oyagi's Method			
	Weight of sample (gm)	Gm of water per gm of dried matter which mixed with $CoCl_2$.	Percentage of the amount of water (gelatin containing $CoCl_2$)	Drying temperature (°C)	Weight of sample (gm)	Gm of water per gm of dried matter which mixed with $CoCl_2$.	Percentage of the amount of water (gelatin containing $CoCl_2$)	Drying temperature (°C)
0	0.9310	1.10	52.1		0.6027	8.35	89.3	
0.5	——	——	——		0.3211	3.99	80	
1.0	0.7714	0.743	42.6		0.2032	2.15	68.3	
1.5	——	——	——		0.1702	1.64	62.1	25°
2.0	0.7408	(H.B.P_2)0.695	41.0		0.1256	0.948	48.7	
2.5	——	——	——	25°	0.1201	0.863	46 3	
3.0	0.6998	0.580	36.7		——	——	——	~
3.5	——	——	——		0.1151	0.785	44	
4.0	0.6752	0.525	34.5		0.1096	(O.B.P_2)0.699	41.1	
4.5	——	——	——	~	0.1079	0.672	40.1	30°C
5.0	0.6556	0.480	32.4		0.1036	0.606	37.8	
5.5	——	——	——		0.1009	0.564	36.06	
6.0	0.6498	0.468	31.9		0.1008	(O.C.P_2)0.564	36.06	
6.5	——	——	——	30°C	0.0780	0.219	17.96	100°
7.0	0.6332	0.430	30.07		0.0645	0.00	0.00	~
7.5	——	——	——		0.0645	0.00	0.00	110°C
8.0	0.6332	0.430	30.07					
8.5	0.6330	(H.C.P_2)0.429	30.02					
9.0	0.5501	0.242	19.46	100°				
10.0	0.4884	0.103	9.33	~				
11.0	0.4429	0.00	0.00	110°C				
11.5	0.4428	0.00	0.00					

The signs of H. B. P_2 or O. B. P_2 shown in Table 1 (Fig. 3) are points at which the color of pieces of dyed gelatine that were treated by Hatschek or Oyagi's method respectively, turns to pure blue from pink color in the course of drying at 30°C. At these points of H. B. P_2 or O. B. P_2 the amount of water estimated in the sample is recognized as the amount of Bound Water. But as shown in this experiment there are other points of H. C. P_2 or O. C. P_2 which are recognized as the apparent constant weight of water in the sample in the course of drying at 30°C from 1 to 3 hours after the appearance of the point of H. B. P_2 or O. B. P_2 (Each sign such as H. B. P_2 or H. C. P_2 has small type figure 2 under the letter P on the right; these figures show the No. 2 of the sample employed. Those

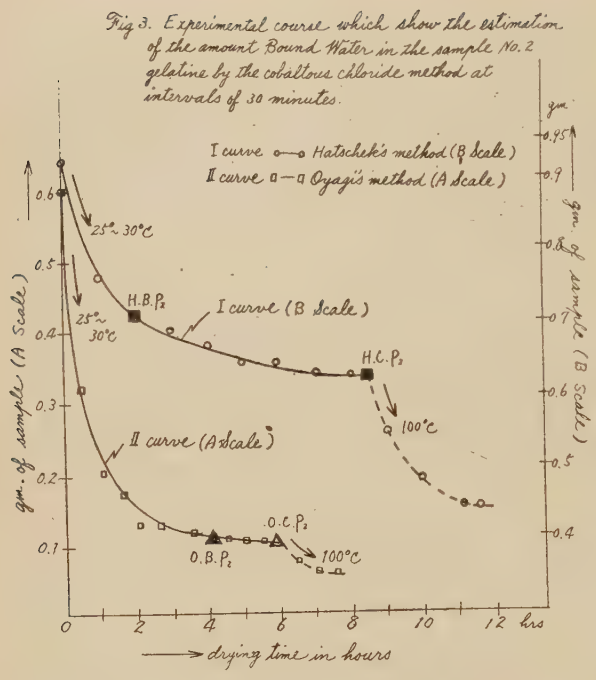


Fig 3. Experimental course which show the estimation of the amount Bound Water in the sample No. 2 gelatine by the cobaltous chloride method at intervals of 30 minutes.

figures that follow are the same).

When the amount of Bound Water is disputed from the point of view of binding strength of water to the colloidal matter, the amount of water in the sample at the point of B. P. (H. B. P or O. B. P) or C. P. (H. C. P. or O. C. P.) which was determined by Hatschek's or Oyagi's method respectively will be recognized as the amount of Bound Water. The author has called the amount of the water estimated at B. P. (H. B. P. or O. B. P.) the maximum value of the amount of Bound Water and the one at C. P. (H. C. P. or O. C. P.) the minimum value of the amount of Bound Water.

Here the author has compared the amount of Bound Water at the points of B. P. (H. B. P. or O. B. P.) and C. P. (H. C. P. or O. C. P.) with the results from the vapour tension method and the method by the electric resistance.

Table 2 shows the amount of Bound Water in the sample of No. 1, No. 2, No. 3 of gelatine by the cobaltous chloride methods.

In considering the difference between the values of the amount of Bound Water in the sample, the difference is owing to the kind of the sample and the initial amount of water in the sample. The estimation of the amount of Bound Water was made by Oyagi's method in Experiment I, II, III, IV, and V about the sample of No. 1 gelatine, air dried sample of No. 2 gelatine, bone dried sample of No. 2 gelatine, air dried sample of No. 3 gelatine, and bone dried sample of No. 3 gelatine respectively. In experiment VI, the author has tried the following treatment according to Hatschek's method: After the addition of cobaltous chloride to gelatine sol having various amounts of water, the mixtures were poured into each cylindrical wooden mold and solidified and then the solidified gelatine was dried at 26°~36°C, the center of the cylindrical dried gelatine was cut off cylindrically at the time of turning blue of the sample. As

the Experiment Ⅶ, the author has employed the Hatschek's method of preparation of sample and Oyagi's method of estimation as follows: Small piece of gelatine gel (the weight of about 0.5 gm) which was added with cobaltous chloride powder was laid on the watch-glass, and was dried at 25°—30°C, and the amount of Bound Water in the sample was estimated. In each experiment, each estimation was carried out in duplicate or triplicate.

In Table 2, the percentage of the total amount of water in the sample after treating with cobaltous chloride (which is written in 5th column of Table 2) is shown as the total amount of water in dyed sample after steeping in cobaltous chloride solution in the case of Oyagi's method, and is shown as the total amount of water in the sample after adding with cobaltous chloride to the sample of gelatine having various amount of water in the case of Hatschek's method respectively.

Table 3 and Fig. 4-1 shows the relation between the vapour tension of the water in the sample, p, (estimated temperature was 13° ± 0.5°C) and the water content of the samples; Fig. 4-2 shows the relation between the water-activity of the samples, "a", and the weight of the amount of the water per gm of the bone dried gelatine of the samples, "g". This relation was obtained from the results obtained by the vapour tension method on No. 2 sample of gelatine, and No. 2 sample of gelatine to which was added cobaltous chloride (the weight of cobaltous chloride was 0.213 gm per gm of dried matter of the mixture). Table 4 and Fig. 5 show the relation between the electric resistance at 50 cycles of frequency and the total amount of the water in the above stated No. 2 samples.

In Hatschek's method the quantity of cobaltous chloride containing 6 molecules of crystal water to be added, is about 50% of the weight of the dried gelatine.

(Ⅱ) Discussion of results on gelatine.

(A) Discussion of results obtained by cobaltous chloride methods.

(a) The comparison of the amounts of Bound Water between sizes and kinds of samples of gelatine by Oyagi's method.

In Experiment Ⅰ of Table 2 which dealt with the sample of No. 1 gelatine, various shapes of gelatine having varied volume and weight were employed, and the experimental results by Oyagi's method shown much the same amount of Bound Water per gm of the dried matter of these samples and shown the mean value of 0.325 gm per gm of dried matter of samples. As shown in Experiments Ⅰ, Ⅲ, Ⅳ, the amount of Bound Water in different kinds of samples of gelatine were recognized to be different.

In conclusion, the amount of Bound Water in various sizes of the sample of

Table 3. Estimating results of the vapour-tension of No. 2 gelatine having various amounts of water at 13°C. ($p_0 = 1.1231$ Hg.cm)

Sample No. 2 of gelatine				Sample No.2 of gelatine containing cobaltous chloride. (The weight of $CoCl_2$ was 0.213gm per gm of bone dried matter of the mixture.)				
Water content in %	gm of water per gm of bone dried gelatine (g_1)	vapour-tension in Hg. cm. (p) 13°C	water-activity of the samples $a = (p/p_0)$ 13°C	water content in %	gm of water per gm of bone dried mixture (g'_2)	gm of water per gm of bone dried gelatine (g_2)	vapour-tension in Hg. cm. (p) 13°C	water-activity of the samples $a = (p/p_0)$ °C
75.0 %	3.01 gm	1.112 cm	0.990	97.8 %	44.5 gm	56.5 gm	1.097 cm	0.977
66.4	1.97	1.109	0.987	88.0	7.33	9.31	1.098	0.977
60.75	1.54	1.102	0.981	80.6	4.15	5.26	1.076	0.958
55.80	1.26	1.087	0.968	65.8	1.92	2.44	1.029	0.916
39.70	0.66	0.989	0.881	59.6	1.48	1.88	1.001	0.891
30.50	0.44	0.886	0.789	56.6	1.30	1.65	1.029	0.915
21.20	0.269	0.707	0.639	48.55	0.945	1.20	0.938	0.836
19.80	0.246	0.518	0.461	45.00	0.820	1.04	0.927	0.825
15.30	0.180	0.196	0.174	36.85 (B.P)	0.584	0.741	0.816	0.726
15.20	0.179	0.163	0.145	33.98	0.515	0.655	0.727	0.647
13.20	0.152	0.041	0.037	31.04	0.450	0.572	0.674	0.600
				30.40	0.436	0.554	0.600	0.534
				29.50	0.418	0.531	0.606	0.537
				29.40	0.416	0.528	0.509	0.453
				23.65	0.310	0.394	0.317	0.282

Table 4. Relation between the electric resistance of 50 cycles and the total amounts of water in gelatine.

Sample No.2 of gelatine		No.2 gelatine containing cobaltous-chloride (The weight of $CoCl_2$ was 0.216 gm per gm of bone dried matter of mixture.)	
water content in %	Electric-resistance in KΩ	water content in %	Electric-resistance in KΩ
98.0	2.5	98	0.32
90.0	1.0	90	0.13
85.6	1.1	80	0.08
73.4	1.4	70.8	0.075
70.0	1.5	51.2	0.18
62.2	1.75	40.2	1.28
58.1	2.1	35.6	3.6
56.7	2.3	34.0	4.6
56.0	3.6	32.8	9.5
44.3	20.0	31.4	11.0
38.2	80	30.6	40
35.5	200	29.6	45
30.4	470	28.8	50
29.4	650	28 0	60
27.4	2,400	27.3	90
25.5	10,000		

Note: Order of the specific resistance of distilled water which was used in this experiment was about 10^{-4}Ω at 18°C.
Appearent electric resistance of distilled water was 25kΩ at which poles distance is 2.3cm.

Fig. 4-1. Relation between the vapour tension of water in samples No.2 of gelatine and their water content (Temp = 13°C. $p_0 = 1.1231$ Hg.cm)

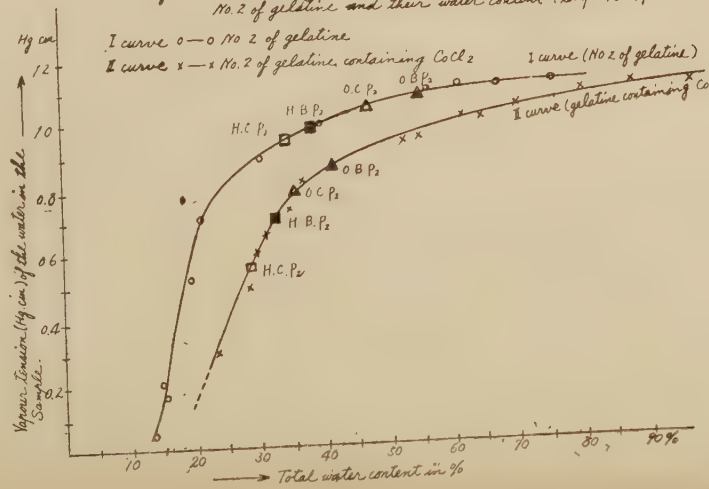
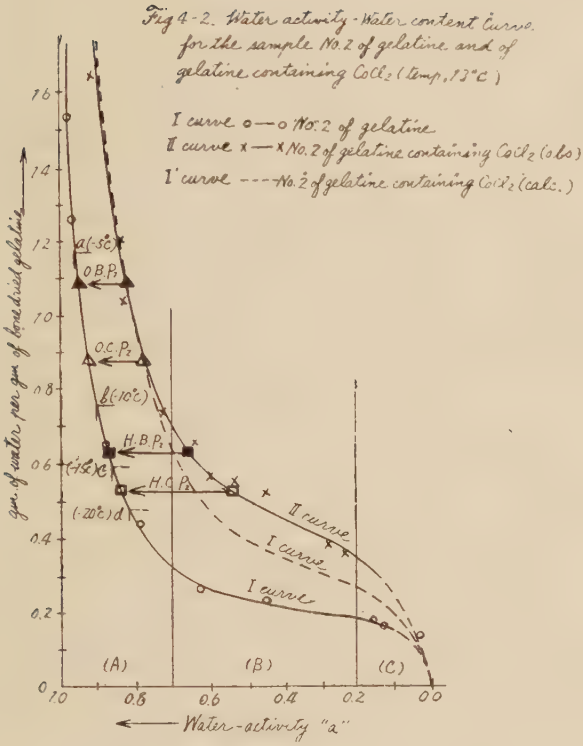


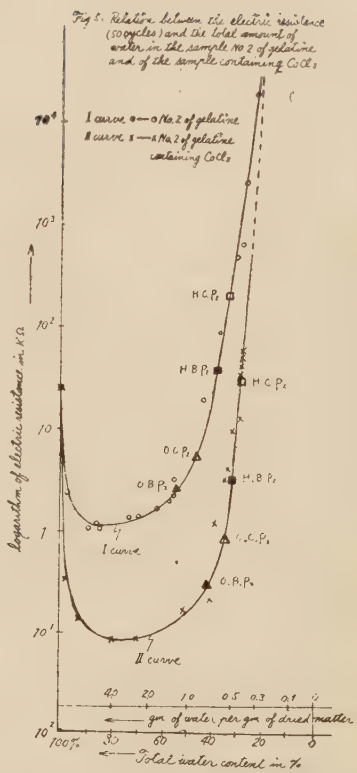
Table 2. Estimating results of the amounts of Bound Water in the Sample No.1, N

Methods	Experiments	Samples		Percentage of the amount of Total Water in the original sample before used.	Percentage of the amount of Total Water after treating with $CoCl_2$.	Calculated from the valu course of drying at 25° (Minimum Valu	
						Percentage of the amount of Free Water after treating with $CoCl_2$	Percentage of the amount of Bound Water after treating with $CoCl_2$.
Oyagi's Method	Experiment I.	Sample No.1	(1)	13.04	83.87	78.77	5.10
			(2)	13.04	85.03	80.04	4.99
			average	13.04	84.45	79.40	5.05
	Exp. II	Sample No.2 (bone dried sample)	(1)	0.00	82.74	74.79	7.95
			(2)	0.00	82.93	74.63	8.30
			(3)	0.00	83.00	74.29	8.71
			(4)	0.00	83.07	75.71	7.36
			av.	0.00	82.94	74.86	8.08
	Exp. III	Sample No.2 (air dried sample)	(1)	17.95	89.51	84.03	5.48
			(2)	17.95	88.92	83.12	5.80
			(3)	17.95	89.31	82.90	6.41
			(4)	17.95	89.30	82.75	6.55
			av.	17.95	89.26	83.20	6.06
	Exp. IV	Sample No.3 (bone dried sample)	(1)	0.00	85.5	80.00	5.50
			(2)	0.00	84.5	79.35	5.15
			av.	0.00	85.0	79.67	5.33
	Exp. V	Sample No.3 (air dried sample)	(1)	18.66	86.1	81.42	4.68
			(2)	18.66	87.1	80.71	6.39
			av.	18.66	86.6	81.06	5.54
Hatsche k's Method	Exp. VI	Sample No.2 pour into the drying mold)	(1)	85.63	82.35	75.49	6.86
			(2)	73.43	69.74	56.44	13.30
			(3)	62.22	56.20	39.00	17.20
			(4)	52.44	48.20	25.94	22.26
			av.	—	—	—	—
	Exp. VII	Sample No.2 (dried on the watch glass)	(1)	85.63	82.35	74.83	7.52
			(2)	73.43	69.74	57.16	12.53
			(3)	62.22	56.20	38.51	17.73
			(4)	52.44	48.20	27.20	21.00
			av.	—	—	—	—

o.2 and No.3 gelatine by the cobaltous-chloride methods. (Hatschek's and Oyagi's Methods.)

es at the apparent constant point (C. P.) in the 30°C. es of the amount of Bound Water)				Calculated from the values at blue point (B. P.) in the course of drying at 25°~30°C. (Maximum values of the amount of Bound Water.)			Remarks.
m of Bound Water per gm of dried matter which was mixed with $CoCl_2$. (g'_1)	Gm of Bound Water per gm of dried matter of gelatine (g_1)	Percentage of the amount of Bound Water in the sample of gelatine-gel.	Gm of $CoCl_2$ per gm of the mixture of gelatine and $CoCl_2$.	Gm of Bound Water per gm of dried matter which was mixed with $CoCl_2$ (g'_2)	Gm of Bound Water per gm of dried matter of gelatine (g_2)	Percentage of the amount of Bound Water in the sample of gelatine.	
0.316	(0.500)	(33.3)	Calculated from the assumption as 0.368	—	—	—	Volume and Weight after ep in 10% Co solution. (1) 1 ×0.3 cm (0.5 (2) 1×1×0.1 (0.1gm)
0.335	(0.530)	(34.6)					
0.325	(0.515)	(34.0)					
0.458	(0.612)	(38)	(0.254)	—	—	—	—
0.486	(0.648)	(39.4)	(0.250)				
0.512	(0.680)	(39.8)	(0.247)				
0.435	(0.581)	(36.7)	(0.252)				
0.473	(0.630)	(38.5)	(0.251)				
0.522	(0.849)	(45.9)	(0.385)	0.710	(1.151)	(57.2)	
0.523	(0.811)	(44.3)	(0.355)	0.665	(1.030)	(51.4)	
0.600	(0.949)	(48.7)	(0.367)	0.766	(1.210)	(54.8)	
0.564	(0.969)	(49.1)	(0.364)	0.699	(1.097)	(54.6)	
0.564(O.C.P'$_2$)	0.894(O.C.P$_2$)	(47.2)	(0.368)	0.710(O.B.P'$_2$)	1.097(O.B.P$_2$)	(54.6)	
0.377	(0.590)	(37.1)	(0.36)	0.453	(0.710)	(41.5)	
0.333	(0.497)	(33.2)	(0.33)	0.385	(0.575)	(36.5)	
0.355	(0.542)	(35.1)	(0.345)	0.419	(0.643)	(39.0)	
0.337	(0.552)	(35.5)	(0.39)	0.645	(1.055)	(52.6)	
0.495	(0.677)	(40.4)	(0.27)	0.419	(0.575)	(36.5)	
0.413	(0.616)	(38.1)	(0.33)	0.532	(0.815)	(44.6)	
0.389	0.516	34.05	0.247	0.484	0.643	39.2	Hatschek h estimated of amoun oft B Water of several kinds gelatine by method. and determined these gelati contained 0. 0.51 gm o Bound Wate gm of dried ple of gela (30.4~34% t dried gelat at the bl turning po
0.439	0.567	36.20	0.225	0.484	0.626	38.5	
0.393	0.500	33.30	0.214	0.493	0.627	38.5	
0.430	0.544	35.20	0.210	0.531	0.673	40.2	
0.413(H.C.P'$_2$)	0.533(H.C.P$_2$)	34.70	0.224	0.491(H.B.P'$_2$)	0.642(H.B.P$_2$)	39.1	
0.426	0.565	36.1	0.247	—	—	—	
0.416	0.538	35.0	0.226				
0.405	0.519	34.2	0.220				
0.405	0.513	33.9	0.210				
0.413	0.534	34.8	0.224	—	—	—	





gelatine were almost the same value within the range of 0.1—0.5 gm of the sample, but the amount of Bound Water was different according to the kinds of samples of gelatine.

(b) The comparison of the amount of Bound Water between the air dried sample and the bone dried sample at 110°C. (by Oyagi's method)

As shown in Experiment Ⅱ, Ⅲ, and Experiment Ⅳ, Ⅴ of Table 2, the amount of Bound Water determined by Oyagi's method in the air dried sample was larger than in the bone dried same sample in a drier at 110°C. In this case, the total amount of water in the air dried sample after steeping it in cobaltous chloride solution was greater than the bone dried same sample in drier at 110°C and the degree of the swelling of the former was also greater than the latter. These results have already been recognized by Lloyd and coinvestigators[4b,c]. And these facts perhaps due to that gelatine which has been dried at 110°C in drier lost water which must have been present as Bound Water in the gelatine during steepng in the cobaltous chloride solution. Therefore the fact that there is some difference according to the kinds of sample, is perhaps caused by the different conditions of drying in the process of manufacturing gelatine.

(c) The comparison of the amounts of Bound Water determined by Hatschek's and Oyagi's methods.

As shown in Experiment Ⅲ and Ⅳ of Table 2, the amount of Bound Water which was determined by Oyagi's method was recognized to be somewhat larger than that of the same sample by Hatschek's method. This is recognized to be due to the different drying mechanisms in both methods.

In Hatschek's method, the quantity of anhydrous cobaltous chloride was mean 0.224 gm per gm of the dried matter of gelatine containing cobaltous chloride powder in a definite proportion as shown in Table 2. That is to say, the quantity of the dried matter of the gelatine was 0.776 gm per gm of the same sample. And in Experiment Ⅲ in Oyagi's method, the quantity of anhydrous cobaltous chloride which penetrated into the sample of gelatine was mean 0.368 gm per gm of the dried matter of the sample of gelatine which was submerged in 10% cobaltous chloride solution. That is to say, the quantity of the dried matter of the gelatine was mean 0.632 gm per gm of the same sample.

Therefore if we show the estimated amount of Bound Water per gm of dried matter of gelatine containing cobaltous chloride by Oyagi's method as the amount of Bound Water per gm of the dried matter of gelatine by Hatschek's method, we must divide the estimated value from Oyagi's method by the quantity of dried matter of gelatine per gm of the dried sample containing cobaltous chloride, for example by the mean value 0.632 above stated, as a factor. The author has given the values thus obtained in parenthesis in the 11th column of Table 2.

From those results by the comparison of the methods of Hatschek and Oyagi, the author has obtained the following conclusion that the values of the amount of Bound Water at the points of B. P. and C. P. by Oyagi's method are larger than values of the amount of Bound Water at the points of B. P. and C. P. by Hatschek's method. That is to say, the amount of Bound Water determined by Oyagi's method is greater than the amount of Bound Water determined by Hatschek's method.

(d) The comparison of the values of the amount of Bound Water obtained by Hatschek's reformed method and the old Hatschek's method.

The values of the amount of Bound Water obtained at the respective point of C. P. in the two different treatments by Oyagi's and Hatschek's methods are almost the same, as shown in each mean value of Experiment Ⅵ and Ⅶ of Table 2. If the purpose of employing the drying mold in Hatschek's method is merely a means to obtain homogeneous drying of sample, the author thinks that it is better to employ a reformed Hatschek's method above stated, because the Hatschek's

method (old) needs a comparatively larger amount of sample and longer time for the estimation of the amount of Bound Water. The reformed Hatschek's method is the most simple in treatment of samples. Moreover the results (Experiment Ⅶ of Table 2) obtained by the process of the reformed Hatschek's method agreed with the value by Hatschek's method (old), so that it is a useful method to determine the amount of Bound Water in samples.

(c) The comparison of the amount of Bound Water between the different initial concentrations of gel of gelatine in the Hatschek's method.

The author was unable to recognize any difference in the values of the amount of Bound Water in the sample of gelatine of which initail concentrations are different in the Experiment Ⅵ. But he was able to recognize the following difference from the results of Experiment Ⅶ that the less the water content of gel of gelatine becomes (i. e. the larger the concentration of gel of gelatine), the less the amount of Bound Water is estimated. The difference of the amount of Bound Water in samples of gelatine having different concentrations of gel has been recognized by Jones and Gortner[6a] according to the dilatometric method, and by Frick[27] according to the method by estimating the dielectric constant. They agreed that the larger the concentration of gelatine becomes, the less the amount of Bound Water in gelatine becomes. The fact that by the cobaltous chloride method which is completely different from the dilatometric method and method by estimating dielectric constant in their principle, much the same result was obtained as the results by the author's method, is very interesting. Therefore in Hatschek's method the same sample having different water content at the time of sampling shows not necessarily the same result.

(B) The comparison of results of the estimated amount of Bound Water by vapour tension method and cobaltous chloride methods (Hatscheh's and Oyag's methods).

In Fig. 4-1, the curves Ⅰ and Ⅱ show the curves of the depression of vapour tension in proportion to the decreasing of the water content of the sample of No. 2 gelatine, and the same sample to which was added cobaltous chloride, respectively. H.B.P_2 (H.B.P_2'), H.C.P_2 (H.C.P_2') and O.B.P_2 (O.B.P_2'), O.C.P_2 (O.C P_2') which are shown on the curves Ⅰ and Ⅱ indicate the points which show the maximum value and minimum value of the amount of Bound Water calculated from the values estimated at B. P. and C. P. according to the Hatschek's and Oyagi's methods respectively. Mean values which were calculated from the amount of Bound Water per gm of dried matter of gelatine containing cobaltous chloride are

written in the 8th and the 12th columns of Experiments Ⅲ and Ⅳ of the Table 2, and are plotted on the curve Ⅱ.

As shown on the curve Ⅱ, the vapour tension decreased at first gradually in proportion as the total amount of water in the sample decreased, and it decreased more rapidly at the points showing the Bound Water content of the sample estimated by cobaltous chloride methods.

In fact, when the water content of the sample of gelatine containing cobaltous chloride reached 36.85% (at neighbouring point of O. C. P_2') as shown in the 5th column of Table 3, the sample has been observed to turn to pure blue.

When the observed values of the amount of Bound Water in the sample shown on the curve Ⅱ are converted into the values of the amount of Bound Water per gm of dried gelatine without cobaltous chloride(as shown as mean values in Experiments Ⅲ and Ⅳ in 9th and 13th columns of Table 2), the points showing the observed values on the curve Ⅱ will be able to be transferred to the curve Ⅰ. Points which were transferred on to the curve Ⅰ from the curve Ⅱ are shown as H. B. P_2, H. C. P_2 and O. B. P_2, O. C. P_2 respectively.

It is clear from Fig. 4-1 that these points on the curve Ⅰ give the values which are considered as the amount of Bound Water in the sample by means of the cobaltous chloride methods even before the sudden depression of vapour tension happens.

The relation between the points on the curve Ⅰ and Ⅱ can be understood as follows : for example, when we added cobaltous chloride to the gelatine which has the water content as much as O. B. P_2 on the curve Ⅰ (the quantity of cobaltous chloride ($CoCl_2 . 6H_2O$) added to the dried gelatine is 50 %) as stated above), the water content of the gelatine which was added with cobaltous chloride decreases to the water content at O. B. P_2' on the curve Ⅱ, and the vapour tension also depresses until the vapour tension at the point O. B. P_2' on the curve Ⅱ. In Fig. 4-2, the curve Ⅰ shows the water-content—water-activity curve for No. 2 of the sample, and the curve Ⅱ shows the water-content—water-activity curve for No. 2 of the sample to which was added cobaltous chloride powder. The reason to believe that the water-content—water-activity curve for the gelatine to which are added cobaltous chloride will be shown as the curve Ⅱ, is because the quantity of cobaltous chloride which penetrates into the sample in the case of Oyagi's method is almost equal to the quantity of cobaltous chloride which is added to the sample in the case of Hatschek's method. Thus points of B. P. and C. P. which were obtained by the cobaltous chloride methods were plotted on the curve Ⅱ in Fig. 4–2.

The water-content per gm of dried gelatine is shown on the ordinate of Fig. 4–2, therefore points which were plotted on the curve II can be transferred horizontally on to the curve I. In Fig. 4-2, the water activity "a" corresponding to the range of the curve I which is recognized as the amount of Bound Water in the gelatine without cobaltous chloride by means of the cobaltous chloride methods was between 0.95 and 0.85.

However, the water-activity "a" corresponding to the range of the curve II which is recognized as the amount of Bound Water in the gelatine to which is added cobaltous chloride decreased to between 0.85 and 0 5, because the water activity decreased owing to the existence of cobaltous chloride in the gelatine.

The water-content—water-activity curve was formerly discussed by Katz[10a], Moran,[7] Brooks[10d] or Briggs[10b,c] and recently by Higashi[1], but it is difficult to decide what range of the curve is the boundary of Free Water and Bound Water, because the ideas for Bound Water are different from the stand points of Biology, Colloidal chemistry and Molecular theory respectively.

However, as a characteristic of the curve of S shape, the water-content—water-activity curve has generally three parts, A, B, C. The part of B is a gentle grade and its range is 0.2—0.7 of the values of "a" that is to say, the variation of the water-content of the sample of gelatine is small. The part of A and C are steep grade and the range of the part A is 1.0—0.7 of the values of "a" and the range of the part C is 0.2—0.0 of the values of "a".

(a) Discussion of the amount of Bound Water from the standpoint of Molecular theory.

In the discussion of the amount of Bound Water from the standpoint of Molecular theory according to Herman, Gerngroß and Abitz[23] and Katz and Derkson[29] who have examined independently the gelatine containing various amounts of water from the defraction by X-ray and Sponsler, Bath and Ellis[3b] who have examined the hydration of water molecules of amino acids which are components of gelatine, it is considered that 0.5 gm of the water-content is at least necessary to constitute molecules of gelatine. According to Adair and Callow[30], the amount of Bound Water is independent of the water-activity, and it takes a definite value of 0.5.

Briggs[10b,c] said that when the water-activity "a" is below 0.8—0.7, water corresponding to that water-activity does not act as a solvent. Recently Bull[31] has examined the relation of water-content—water-activity of gelatine and other various high molecular compounds, and analyzed his results by the equation of

B. E. T.[32] He has discussed water whose activity is below 0.7 of water-activity "a".

From analyzed result of the curve I and II in author's experiments using the equation of B. E. T., about 0.35 gm and about 0.7 gm of the water-content per gm of the dried gelatine respectively were considered to be necessary to saturate each hydrating point in the molecule of gelatine. But the author will in detail report elsewhere.

Here, however, the author wishes to have an opportunity to say the following: about 0.35 gm of the water content per gm of the dried gelatine in the case of the curve I, and about 0.7 gm in the case of the curve II correspond respectively to about 0.7 of the water-activity "a".

From thinking thus, the amount of Bound Water at the point of H. C. P_2 on the curve I by means of Hatschek's method will give the approximate value of the amount of Molecular theoretical Bound Water. The amounts of Bound Water at the point of O. B. P_2, O. C. P_2 and H. B. P_2 are Bound Water having some weak binding strength, that is to say, it has more or less properties of Free Water.

(b) Discussion from the standpoint of colloidal chemistry on Bound Water.

Next the author will discuss from the standpoint of colloidal chemistry. In the case of the determination of the relation of water-content—water-activity by the method by the depression of freezing point and the calorimetric method the water-activity "a" varies according as the variation of freezing point of the sample (T'°K), and the water-activity of the sample is calculated from the following equation (1) under the assumption that colloidal matter has generally no heat of dilution[33].

$$\log a = -0.004211\,(273.1-T') + 0.0000022\,(273.1-T')^2 \text{----(1)}$$

From equation (1), the relation between the water-activity and freezing point of pure water will be calculated as Table 5.

Table 5. The relation between the water activity and freezing point of pure water.

Water-activity "a"	Freezing point °C
0.9526	− 5
0.9071	−10
0.8630	−15
0.8220	−20

That is to say, the less the water-activity of the sample becomes, the lower the freezing point of the sample is, and the value of the water-activity becomes the approximate value of 1, in proportion as the freezing point approaches to 0°C.

Assuming that water in the sample conforms to the law of true solution, the values of the water-activity corresponding to various freezing points (shown as Table 5) are plotted on the curve I of Fig. 4-2, where they are shown as points of a, b, c, d. From the position of these points, the author knows that

each value of the amount of Bound Water corresponding to each value of the water-activity shows the range extending over the water-contents per gm of bone dried gelatine at the points from "a" (water-activity 0.9526) to "d" (water-activity 0.822). (That is to say, the points correspond to freezing points ; $-5°\sim-20°C$).

In estimating the amount of Bound Water in the gelatine or other colloidal matters by solvent methods (e. g. method concerning the depression of the freezing point) or by Freezing methods (e. g. Calorimetric method, Dilatometric method), the water-content of the samples corresponding to $-5°\sim-20°C$ in the former case and to $-20°C$ in the latter case respectively, were obtained. The amount of Bound Water in the samples according to the cobaltous chloride method is the water-content corresponding to the same range of values of water-activity as the methods stated above. In a word, the values of the amount of Bound Water in the sample estimated by various methods are almost the same.

The water content at points of O. B. P_2, O. C. P_2 which were obtained by Oyagi's method and plotted on the curve I of Fig. 4-2 and the water content at point of H. B. P_2 which was obtained by Hatschek's method and plotted on the curve I, are too large as the amount of colloidal Bound Water. But in Oyagi's method the water content per gm of dried matter containing cobaltous chloride is considered as the amount of Bound Water in pure gelatine as above stated (1) (II) (B), so that if the water-content of 0.564 at O. C. P_2 in the 8th column of Experiment III in Table 2, and 0.710 at O. B. P_2 in the 12th column of Experiment III in the same Table are plotted on the curve I, the point of O. B. P_2' will be situated near the point of H. B. P_2, and the point of O. C. P_2', will be situated near the point of H. C. P_2.

However, since the water content which was looked upon as the amount of Bound Water in gelatine according to the Hatschek's method agreed with the water content which was looked upon as the amount of Bound Water in gelatine according to various other methods, Hatschek has proposed that his method should be employed for the estimation of the amount of Bound Water.

The author has gone a step further and explains as follows : This agreement is due to the fact that the amount of Bound Water in the samples is water having the same water-activity.

The water content at the points of O. B. P_2' and O. C. P_2' are shown as propriately as the amount of colloidal Bound Water from the idea as stated above.

In a word, the values which are obtained from the cobaltous chloride methods are considered to agree rather with the values of the amount of colloidal Bound

Water than with the value of the amount of Molecular theoretical Bound Water.

However, whether the amount of colloidal Bound Water is always larger than the amount of Molecular theoretical Bound Water cannot be determined until the meaninig of molecular theoretical Bound Water is settled.

(c) The influence of addition of salts to the sample in the estimation of the amount of Bound Water.

When the curve Ⅱ of Fig. 4-2 is compared with the curve Ⅰ of the same Fig., the water-activity of the former is smaller than the water-activity of the latter at the same water-content, because the curve Ⅱ is influenced by the addition of cobaltous chloride.

If cobaltous chloride which was added to the sample dissociates 100% and if three ions (viz. one ion of Co^{++} and two ions of Cl^{-}) are dissociated from one molecule of cobaltous chloride, the curve Ⅰ′ will be theoretically formed from the curve Ⅰ according to our calculation as well as to Briggs.[10b]

The theoretical curve of water-activity—water-content is shown as a dotted line (Ⅰ′-curve) in Fig. 4-2.

The water-content "g" per gm of dried gelatine corresponding to various water-activities "a" is measured from the curve Ⅰ of Fig. 4-2, and the freezing point (Δ°C) of water at each water-activity "a" is calculated by equation (1), these values are shown in the 1st, 2nd and 3rd columns of Table 6.

The values in 4th column of Table 6 are the water-content "g" per gm of the gelatine with cobaltous chloride added at the same water-activity as the curve Ⅱ.

The quantity of cobaltous chloride in the sample is 0.213 gm per gm of the dried matter, so that 2.08×10^{-3} Mol of cobaltous chloride is equivalent to 1 gm of the dried gelatine.

Therefore the water-content which is necessary for showing freezing point corresponding to various water-activities "a" in the case of dissolving the quantity of cobaltous chloride as stated above, is calculated from the following equation (2).

$$W=3\times\frac{2.08\times10^{-3}\times10^{3}\times1.86}{\Delta} \qquad \text{----------(2)}$$

The results obtained from the equation (2) are shown in the 5th column of Table 6.

The 6th column of Table 6 shows the total amount of hydrated water in gelatine and hydrated water dissolved in cobaltous chloride. Each water-activity of hydrated water in both materials is the same. The water-activity of this

Table 6. Calculated results of the amounts of water (gm of water per gm of bone dried gelatine) at the each water-activities in the system of No. 2 gelatine, cobaltous-chloride and water. (Temp. = 13°C, p_0 = vapour tension of pure water = 1.1231 Hg. cm.)

Water activity $a = p/p_0$	Freezing point Δ C	A (obs.) Gm of water per gm of bone dried gelatine for the system of No.2 gelatine and water. (enterpolated from I curve in Fig. 4—2)	B (obs.) Gm of water per gm of bone dried gelatine for the system of No.2 gelatine, $CoCl_2$ and water.	W (calc.) Gm of water per gm of dried $CoCl_2$ wihch is able to hydrate with $CoCl_2$.	(A−W) calc. Theoretical amount of water (gm of water per gm of bone dried gelatine) for the system of No. 2 gelatine, $CoCl_2$ and Water.	(A−W)/B Ratio of the calc. and obs. (I′ curve in Fig. 4—2)
0.95	5.2	1.15	——	2.23	——	——
0.90	10.8	0.76	1.80	1.074	1.834	1.020
0.85	16.6	0.56	1.255	0 699	1 259	1.002
0.80	22.6	0.456	0.990	0.514	0.970	0.980
0.75	29.1	0.380	0 808	0 399	0.779	0.965
0.70	36.0	0.330	0.700	0.323	0.652	0.932
0.65	43.3	0.296	0 634	0.268	0 564	0.890
0.60	51.3	0.270	0.586	0 226	0.496	0·847
0.55	59.8	0.253	0.552	0.194	0.447	0.810
0.50	69.0	0.243	0.523	0.168	0.411	0.786
0.45	79.1	0.232	0 492	0.147	0.379	0.771
0.40	90.1	0.221	0.465	0.129	0 350	0.753
0.35	102.6	0.213	0.438	0.113	0.326	0.744
0.30	116.8	0.206	0.410	0.099	0.305	0.745
0.25	134.0	0.198	0.383	0.086	0.294	0.769
0.20	148.2	0.189	0.363	0.078	0.267	0.736
0.15	174	0.179	0.322	0.067	0.245	0.761
0.10	210	0.165	0·267	0.055	0.220	0.824
0.05	270	0.128	0.185	0.043	0.171	0.925
						average 0.848

total amount of hydrated water is considered as the water-activity of the system of gelatine, cobaltous chloride and water. The 7th column of Table 6 shows the comparison of theoretical values which are calculated as above stated and the observed values.

According to Table 6 and Fig 4-2, the theoretical curve and the observed curve are the same when the values of water-activity "a" are in the range of 1.0—0.8, but when the values of water-activity "a" are below 0.8, the ratio of the theoretical value to the observed value of water-content is below 0.95. Therefore it is seen that curve I′ slips gradually down from the curve I.

But it is a noteworthy fact that the depression of the freezing point of the concentrated electrolyte solution is not necessarily proportional with the increasing of its concentration, as often observed. That is to say, the high concentrated solution of electrolytes shows usually abnormal depression of freezing point (abnormal depression of the water-activity "a"). For example Rudorff[34] has estimated the freezing point of various kinds of high concentrated solutions of cobaltous chloride, and his results are shown in the Ist and 3rd columns of Table 7.

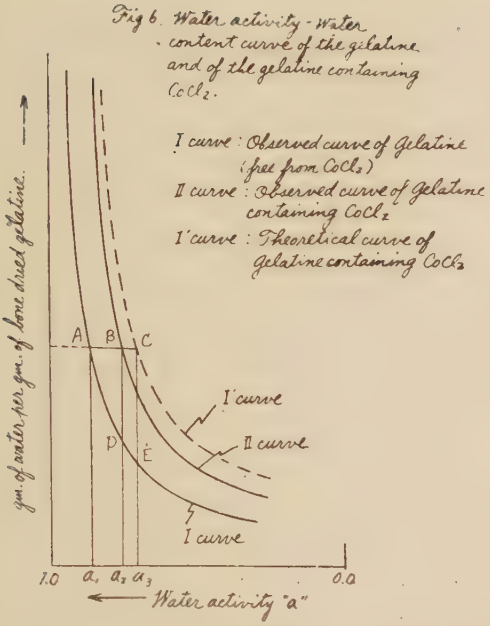
Table 7. Relation between the freezing point (or water-activity) and the amount of hydrated water in the various concentration of cobaltous-chloride ($CoCl_2 \cdot 6H_2O$) solution. (Rudorff)

Gm of $CoCl_2 \cdot 6H_2O$ per 100gm of water	W (obs.) Gm of water per 0.2706 gm of $CoCl_2$	A (obs) Freezing point Δ°C	Water-activity at A	W′ (calc.) Gm of water per 0.2706 gm of $CoCl_2$	A′ (calc.) Freezing point Δ°C	Water activity at A′	Ratio of calc. and obs. W′/W=A′/A	Ion number (degree of ionization)
10	5.18	2.05	0.980	5.66	2.24	0.978	1.092	2.74
20	2.71	4.50	0.956	2.58	4.28	0.960	0.952	3.15
30	1.88	7.35	0.930	1.58	6.17	0.941	0.840	3.57
40	1.47	10.35	0.905	1.12	7.90	0.926	0.762	3.94
50	1.215	13.80	0.874	0.84	9.55	0.911	0.692	4.32
60	1.05	16.80	0.848	0.69	11.04	0.899	0.657	4.56

The 2nd column of the Table 7 shows the amount of water "W" which is added to 2.08×10^{-3} Mol of cobaltous chloride to prepare the concentration of cobaltous chloride solution used by him,

The values in the 4th column are shown as the values of water-activity corresponding to the measured freezing points from the equation (1). W′ in the 5th column and A′ in the 6th column of the Table 7 are the water-content and freezing point (Δ°C) respectively which are calculated theoretically from the equation (2). The values in the 7th column of Table 7 are shown as the ratio of theoretical value to observed value. According to Table 7, when the water-activity "a" is below 0.956, the ratio of Calc./Obs. becomes gradually smaller, and when the water-activity is about 0.85, the ratio is about 0.66. On the contrary, in order to make the theoretical value agree with the observed value, the number of ions, 3, shown in the equation (2) should apparently be increased more than 3 in proportion to the increase of the concentration of the cobaltous chloride solution. But the more the concentration of the electrolyte increases, the less the electrolytic dissolubility becomes, so that the number of ions necessary is not considered more than 3.

After all, in high concentrated cobaltous chloride solution the fact of abnormal depression of freezing point (or the fact of abnormal depression of vapour tension) is observed as well as the presence of Bound Water in colloidal solution. Therefore the theoretical value does not agree with the observed value, that is to say, the curve I′ in Fig. 4-2 does not fit in with the practical case, and when the water-activity "a" is below 0.9, the water-content—water-activity curve which will theoretically agree with the observed value slips from the curve I′ as shown in Table 6, so that, this curve is properly considered as slipping down to the right hand of the curve I′ and II at the same amount of water. (slipping down at upper position at the same water-activity.)



In Fig. 6 the curve I is the system of gelatine and water, the curve II is the system of gelatine, salts and water, and the curve I′ is the curve which will theoretically agree with the curve II of gelatine containing cobaltous chloride. The water-activity (or the freezing point Δ°C) of the hydrated water in gelatine and the hydrated water in salts are supposed to be the same even after the mixing of gelatine with cobaltous chloride as stated above.

Now, the author calls the point A which indicates the water-content per gm of dried gelatine corresponding to the water activity a_1 on the curve I; and also the points of juncture of the straight line which is drawn horizontally from A against a-axis (abscissa) with the curve II and I′, he calls B and C respectively. The water-activities corresponding to B and C are a_2 and a_3. The author calls the points of juncture of straight lines of a_2-B and a_3-C with the curve I, D and E respectively. As the ordinate of Fig. 6 indicates the water-content (gm) per gm of bone dried gelatine, the water contents at the points of A, B, C are of course the same. Therefore, when a definite quantity of cobaltous chloride is added in to the system of gelatine and water having water-content corresponding to the point of a_1 of the water-activity, the water-activity "a_1" drops theoretically to "a_3" by influence of the existence of the salt. If the curve II agrees with the curve I′, according to the ideas of Newton and Gortner[8a] or Hill[9] that Bound Water does not act as a solvent, the water-content between the points of C and E will be Free Water and the water-content between the points of a_3 and E will be Bound Water, but the water-activities of both waters will equally be a_3.

However, the curve II does not agree with the curve I′, the system of gelatine containing salts and water is shown as the curve II as above stated, so that the normal depression of water-activity ($a_1 \rightarrow a_3$) (the depression of freezing point according to Newton and Gortner; the depression of vapour tension according to Hill) does not take place, but the water-activity drops practically to a_2.

From considering these phenomenon, if there is a definite quantity of Bound Water in a system at the point of a_1 of the water-activity, (supposing that gelatine combines with water having a definite binding strength corresponding to the water-activity of gelatine), all the quantity of added cobaltous chloride will combine not only with Free Water in the system, but also with a part of water bound with gelatine. But it will not combine with all the water corresponding to the water-content between the points of C and E which will be considered as Free Water, in other words, it will combine practically with Free Water corresponding to the water-content between the points of B and D. The reason for this is that the stronger the binding strength of Bound Water for gelatine becomes in proportion to the depression of the water-activity, the less the strength of hydration of the added cobaltous chloride becomes. This fact is also owing to another reason, that not all of the added cobaltous chloride takes a part of the hydration, that is to say, a part of it precipitates as solid in the system, and the rest alone hydrates with hydratable water (e.g. water corresponding to the water-content between the points B and D) and indicates the water-activity "a_2". The rest of the water which is not bound with cobaltous chloride is water combining with gelatine, this water indicates also the same activity "a_2". So that whole system indicates the same water-activity "a_2". That is to say, the system of gelatine and salt solution consists of the following three systems at eutectic point of the mixture of the samples. (1) Gelatine and water which combines with gelatine, (2) Salt and water which hydrates with salt. (3) Precipitated salt.

There are probably some questions about the consideration of salt and gelatine that are unable to be explained from the author's experiments. but the author intends to explain these question by further experimental results later on.

(C) Results from the estimation of the amount of Bound Water in the gelatine by cobaltous chloride method and these results were compared with the results from the method by electric resistance.

The curves I and II of Fig. 5 show the relation between the water content of No. 2 sample of gelatine and the same sample containing cobaltous chloride (the same sample as employed in the estimation of vapour tension) with 50 cycle resistance respectively. The ordinate of Fig. 5 shows logarithms of values of electric resistance (kilo-ohm), the abscissa shows the water-content ($^0/_0$) of the samples.

As shown in these two curves, the less the water-content of the sample

becomes, the less gradually the electric resistance decreases, but the electric resistance starts gradually increasing at 70～80% of the water-content. The electric resistance increases suddenly from the water-content at the point of O. B. P_2, but it is difficult to measure such low frequency of electric resistance as that below the water-content corresponding to the point of H. C. P_2. This fact will be understood by the following considerations: as stated at (B), the value of the amount of Bound Water estimated by cobaltous chloride methods gives the amount of colloidal Bound Water, and it takes a part of the affinity of intermolecules, and it does not act as a solvent of salts or other existing substances in the sample. On this subject, Robinson[1a] has stated that the greater the amount of Bound Water is in the sample, the less the electric conductivity becomes.

The less the water-content in the gelatine containing cobaltous chloride becomes, the higher the concentration of electrolyte becomes. As shown in the curve Ⅱ, the increasing of electric conductivity and the decreasing of electric resistance are seen in the first course of the decreasing of water-content of the sample. But when the concentration of gel increases further, and Free Water in the total amount of water of the sample decreases, that is to say, the amount of Bound Water proportionally increases (This fact is clear from experiment Ⅳ of Table 2), it is considered that there is a point which shows the maximum amount of Bound Water in the course of increasing of the concentration of gel. At that point, the electric resistance decreases to the minimum point

With the decreasing of water-content in the sample, if the state of water becomes to molecular Bound Water from the colloidal Bound Water, the electric resistance is considered to increase suddenly. The curve Ⅱ shows that this explanation is right.

As shown in the curve-I, the depression of electric resistance of the first step in accordance with the decreasing of water-content is considered to be owing to the increase of the concentration of electrolyte from the reason that the sample has 0.52% of electrolyte as NaCl in ash, and the sample was not iso-electric protein. Frick[27] has investigated the relation between the gel concentration and dielectric constant (ε) in the wide range of wave lengths, his result was that the dielectric constant (ε) is the maximum at 40% of the concentration of gel. Recently, Takeda[35] has discussed Frick's result and has concluded that the decreasing of dielectric constant (ε) is owing to the decreasing of the amount of Bound Water. As stated in (A), Newton and Gortner[8a] have investigated

on Bound Water in gelatine by Dilatometric method and the present author has investigated the same subject by Cobaltous chloride methods and they have admitted that the greater the concentration of gel is, the less the amount of Bound Water becomes. From these results, the fact that when the total amount of water decreases below 60% in the sample, the electric resistance increases, is owing to the decreasing of the amount of Bound Water. Because water which has strong binding strength rests only in the sample.

Sheppard, Houck and Dittmar[35] have investigated the electric conductivity of gelatine. From their result, it was clear that the gelatine shows the minimum electric conductivity at its isc-electric point, and the less the amount of water in the sample becomes, the less the electric conductivity becomes, and the relation between the water content of below 20% and the logarithm of electric conductivity shows a straight line. The author has considered that when the total amount of water in the sample is below 20%, the electric resistance increases proportionally to the decreasing of the amount of water.

At last, the fact of the decreasing of electric resistance at the initial decreasing of water-content in the curves of Fig. 5, is explained from the physical consideration besides the upper mentioned consideration as follows: when the concentration of gel increases, the so called "water-channel" which is temporarily charged with electricity will be formed between mycels of gelatine, and therefore the electric conductivity will increase and the electric resistance will decrease

When water which existed in mycels (this is considered as Free Water) evaporates out in accordance with increasing of the concentration of gel, that is to say, when only Bound Water remains in the sample, the electric resistance is considered to increase.

From considering thus, even if the employed sample was isoelectric protein, the electric resistance will be considered to decrease temporarily at the initial decreasing of water-content in the curves of Fig. 5. But this consideration will not yet be conclusive by the author's results at this time.

It is of interest that the physical state of water in the sample can be determined from the estimation of such lower frequency of electric resistance.

(3) Experimental results on the fish meat muscle.

(1) Results from the estimation of the amount of Bound Water in the fish muscles by the cobaltous chloride method were compared with the results from the vapour tension method and the method by electric resistance.

Table 8 and Fig. 7 are the experimental course showing the amount of Bound Water in Hatahata-fish (Sandfish : *Arctoscopus japonicus STEINDACHNER*) by cobaltous chloride method (Oyagi's method) at intervals of 30 minutes.

In the case of the estimation of the amount of Bound Water in the fish meat muscle by Oyagi's method, it is observed that there is the maximum value of the amount of Bound Water which is estimated at the point of B. P. (O. B. P.) in drying (at 30°C) of dyed fish meat muscle by cobaltous chloride solution and the minimum value of the amount of Bound Water which is estimated at the point of C. P. (O. C. P.) as well as in the case of gelatine. The author has estimated two values of the amount of Bound Water at both points, B. P. and C. P., and has compared them with other methods.

Table 9 shows the results of the estimated amount of Bound Water in fresh Sandfish, Atka Mackerel, and Squid by cobaltous chloride methods. The experimental results by Oyagi's method are shown as gm of water-content per gm of dried matter containing cobaltous chloride. Table 10 shows the relation among the vapour tension, the water-content and the water-activty of the fresh Atka Mackerel meat and the same meat containing cobaltous chloride powder (about 50% of $CoCl_2 \cdot 6H_2O$ powder was added to the dried matter of fish meat by Hatschek's method). Table 11 shows the experimental results of vapour tension in Sandfish meat and Squid meat muscle. Fig. 8 shows the curve of the depression of vapour tension in accordance with the decreasing of water-content (%) of samples, which were written in Table 10 and 11.

Fig. 9-1 shows the relation between the water-content "g" and the water-activity "a" in Atka Mackerel meat muscle (the amount of water-content "g" (gm) per gm of dried fish meat muscle).

Fig. 9-2 shows the relation between the water-content "g" and the water-activity "a" in Sandfish meat and Squid meat which were written in Table 11.

Table 12-1 and Table 12-2 show the relation between the electric resistance of 50 cycles and the water-content in Atka Mackerel and Squid meat muscle. These reults are shown in Fig. 10-1, Fig. 10-2.

(II) Discussion on the experimental results of the fish meat muscle.

(A) Experimental results of Bound Water by the cobaltous chloride method.

When we compare the experimental results by Oyagi's method with these Hatschek's method about Atka Mackerel meat in Table 9, the amount of Bound Water per gm of dried matter "g" at B. P., (Blue turning point) by Oyagi's

Table 8. Experimental course which show the variation of the amount of water at intervals of 30 minutes in the drying of Sandfish meat muscle by the cobaltous-chloride method. (Oyagi's method)

Drying time in hrs.	Weight of sample (gm)	Gm of water per gm of dried sample which was mixed with cobaltous chloride (gm)	Water-content in %	Temperature (°C)
0	0.1561	5.99	85.7	
0.5	0.0651	1.91	65.6	25°
1.0	0.0514	1.31	56.8	
1.5	0.0413	0.86	46.3	
2.0	0.0372	0.67 (O. B. P)	40.1	~
2.5	0.0360	0.62	38.2	
3.0	0.0340	0.53	34.6	
3.5	0.0304	0.37	27.0	30°C
4.5	0.0302	0.356 (O. C. P)	26.3	
5.0	0.0251	0.130	11.5	100°
5.5	0.0223	0.00	0.00	
6.0	0.0223	0.00	0.00	~ 110°C

Table 9. Estimating results of the amount of Bound Water in the fresh Atka Mackerel, Sandfish and a Sqiud meat muscles by the cobaltous-chloride methods. (Hatshek's and Oyagi's Methods)

		Atka Mackerel (HOKKE; *Plourogrammus azous JORDAN et METZ*)		Sandfish (HATA-HATA; *Arctoscopus japonicus STEINDACHNER*)		A species of Squid (YARI-IKA; *Loligo bleekeri KEFERSTEIN*)	
		Gm of Bound Water per gm of dried matter which was mixed with $CoCl_2$.	Percentage of the amount of Bound Water.	Gm of Bound Water per gm of dried matter which was mixed with $CoCl_2$.	Percentage of the amount of Bound Water.	Gm of Bound Water per gm of dried matter which was mixed with $CoCl_2$.	Percentage of the amount of Bound Water.
Oyagi's Method	The maximum value of the amount of Bound Water at O.B.P.	0.961 gm (O.B Pa)	49%	0.670 (O.B.P_b)	40.1	——	——
	The minimum value of the amount of Bound Water at O.C.P.	0.372 (O.C.Pa)	27.1	0.356 (O C.P_b)	26.2	(1) 0.417 (2) 0.536 average 0.477 (O.C.Pc)	29.4 34.9 32.3
Hatschek's Method	The maximum value of the amount of Bound Water at H. B. P.	0.420 (H.B Pa) The amount of Bound Water (gm) per gm of dried sample is 0.539gm (35%)	29.6 The weight of $CoCl_2$ was 0.221 gm per gm of dried matter of mixture.	——	——	——	——

Table 10. Estimating results of vapour-tension of Atka mackerel meat muscles having various amounts of water at 15°C.
($p_0 = 1.2788$ Hg. cm)

Atka Mackerel meat (sample I.)				Atka Mackerel (II) (Cobaltous chloride added to the sample I. The weight of $CoCl_2$ was 0.221gm per gm of dried matter of mixture)									
Water content in %	Gm of water per gm of bone dried meat muscle (g_1)	Vapour tension in Hg·cm (p) 15 C	Water activity of the samples (a) 15°C	Water content in %	Gm of water per gm of bone dried matter of mixture (g'_2)	B (obs.) Gm of water per gm of bone dried meat muscles (g_2)	Vapour tension in Hg·cm (p′) 15°C	Water activity of the samples (a′) 15°C	Freezing point (Δ°C)	W (calc.) Gm of water which will be able to hydrate with $CoCl_2$	A (obs.) Gm of water which was enterpolated from $g_1 - a$ curve	(W + A) calc. Theoretical amount of water (gm of water per gm of bone dried meat muscles) which containing $CoCl_2$ sample.	(W + A)/B Ratio of calc. and Obs.
78.3	3.61	1.274	0.996	38.1	0.616	0.792	0.956	0.748	29.3	0.415	0.38	0.795	1.004
60.0	1.50	1.194	0.934	25.8	0.348	0.447	0.763	0.597	51.7	0.235	0.223	0.458	1.023
39.3	0.646	1.079	0.844	18.8	0.231	0.297	0.623	0.487	71.2	0.171	0.169	0.340	1.145
25.4	0.341	0.932	0.729	17.8	0.216	0.278	0.514	0.402	89.9	0.135	0.146	0.281	1.010
17.3	0.209	0.691	0.540	15.1	0.178	0.229	0.439	0.343	104.5	0.116	0.141	0.257	1.1210
12.9	0.148	0.317	0.405	14.4	0.168	0.216	0.374	0.293	119	0.102	0.138	0.240	1.1110
10.9	0.122	0.256	0.210	13.1	0.151	0.194	0.371	0.290	120	0.1013	0.137	0.238	1.228
10.0	0.111	0.130	0.102	——	——	——	——	——	——	——	——	——	average 1.092

Table 11. Estimating results of vapour-tension of the fresh Sandfish and Squid-meat muscles having various amount of water at 15°C
($p_0 = 1.2788$Hg . cm)

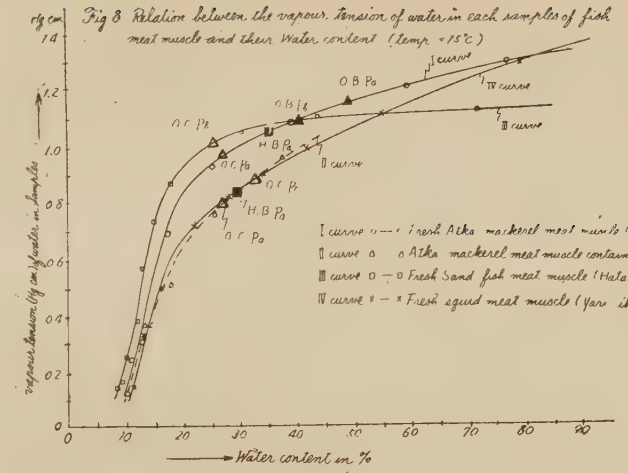
Sandfish meat muscle				A species of Squid meat muscle			
Water content in %	Gm of water per gm of bone dried matter (g'_3)	Vapour tension in Hg·cm (p″) 15°C	Water activity of the sample (a″) 15 C	Water content in %	Gm of water per gm of bone dried sample (g'_4)	Vapour tension in Hg·cm (p‴) 15°C	Water activity of the sample (a‴) 15°C
72.6	2.66	1.110	0.867	80.13	4.03	1.272	0.995
44.4	0.79	1.090	0.853	70.06	2.33	1.208	0.945
31.1	0.45	1.042	0.816	55.88	1.26	1.102	0.862
17.9	0.22	0.870	0.680	42.31	0.734	0.978	0.765
15.2	0.180	0.745	0.582	34.50	0.527	0.894	0.699
13.1	0.150	0.574	0.449	28.17	0.392	0.815	0.638
11.8	0.133	0.388	0.303	22.30	0.287	0.710	0.555
9.84	0.109	0.261	0.204	16.40	0.196	0.503	0.394
9.11	0.100	0.175	0.137	13.26	0.152	0.327	0.256
8.16	0.088	0.155	0.123	11.27	0.127	0.144	0.113

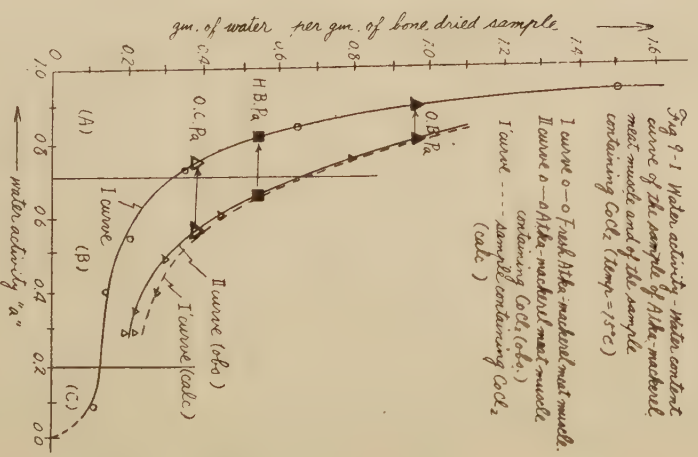
Table 12. 1. Relation between the electric resistance at 50 cycles and the total amount of water in the fresh Atka Mackerel meat muscles.

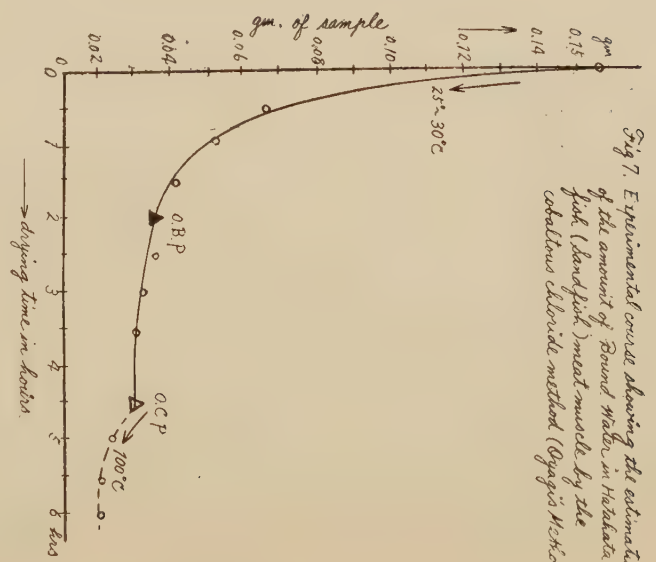
Percentage of total water (%)	Gm of water per gm of dried matter (gm)	Distance of poles and electric resistance in KΩ		
		1.5 cm	2.0 cm	3.0 cm
80	4.0	0.450	0.520	0.710
70.3	2.36	0.410	0.470	0.550
48.4	0.937	0.450	0.630	0.760
38.2	0.618	0.650	0.870	1.150
30.0	0.428	1.02	1.45	2.2
24.5	0.324	5.5	7.5	10.0
20.2	0.253	60	160	170
14.8	0.174	1000 over	——	——

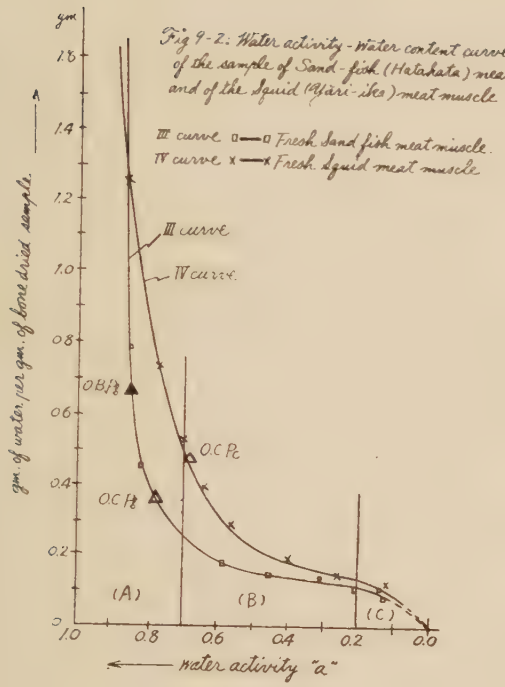
Table 12—2. Relation between the electric resistance at 50 cycles and the total amount of water in the fresh Squid meat muscles. (Pole-distance was 1.5cm)

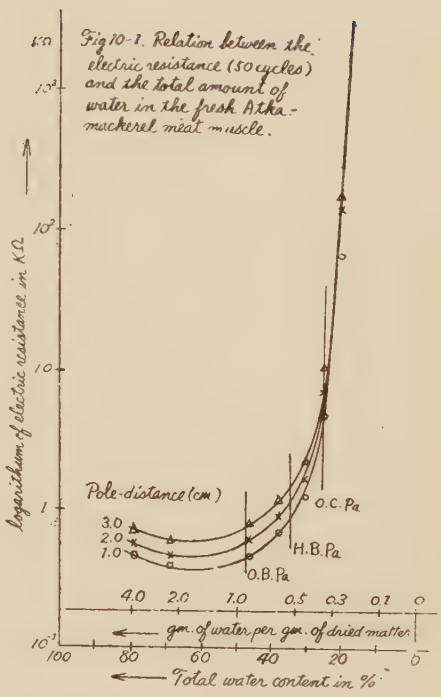
Percentage of total water (%)	Electric resistance (K Ω)
79.86	0.77
58.6	1.07
33.5	2.5
26.0	15
22.98	25
22.35	35
20·26	46
18.65	90
15.8	360
13.0	700

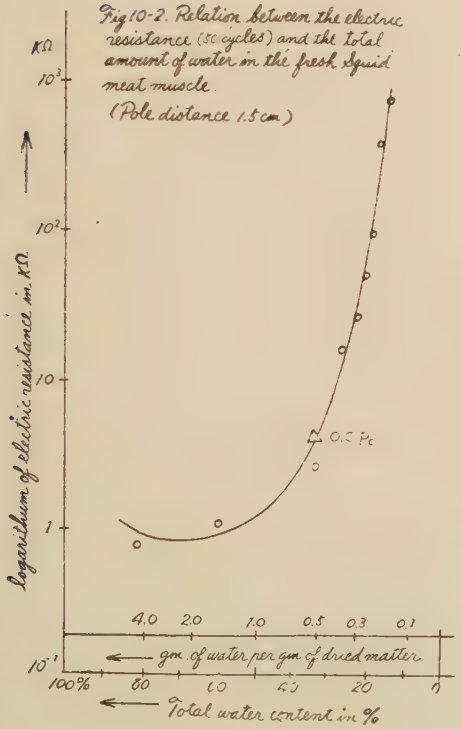












method is greater than by Hatschek's method. This result is the same as in gelatine. This difference is owing to the different condition of fish meat muscle tissue treated by Oyagi's and by Hatschek's methods.

Therefore the mechanism of evaporation of water from the fish meat is of course different. In general, the fish meat treated by Hatschek's method is ground meat, and its tissue is comparatively rough, therefore the evaporation of water from the fish meat is uniformly done. Therefore the time of turning of pink color to blue color from the environment of the sample to the center is short, and excess drying takes place. But it is more difficult to identify the blue turning point in the estimation of Bound Water by

Hatschek's method with fish meat muscle than with gelatine.

(B) The comparison of the results of vapour tension with the results of cobaltous chloride method.

The curves I and II of the relation between the water-content and vapour tension of fish meat muscle shown as in Fig. 8 are the curves for Atka Makerel meat and for the same meat containing cobaltous chloride (0.221 gm of cobaltous chloride per gm of dried fish meat) respectively.

H. B. P_a and O. C. P_a are situated before the sudden change of depression of vapour tension on the curve II. Each sign such as H. B. P_a or O. C. P_a have small type figure "a" under the letter P on the right, those figures show the kind of fish, e.g. Atka Mackerel. Those figures that follow are the same. H. B. P_a of the curve II which indicates the amount of Bound Water will be transferred on to H. B. P_a on the curve I, when the amount of Bound Water of Atka Mackerel meat will be calculated for the same meat containing no cobaltous chloride. This point of H. B. P_a of the curve I corresponds to the value of the amount of Bound Water of 0.539 gm (35%) per gm of dried meat which is written in the 3rd column in Table 9.

The amount of Bound Water which was estimated by Oyagi's method is shown by the amount of Bound Water per gm (g′) of sample containing cobaltous chloride, therefore as shown in the sample of gelatine, O. C. P_a and O. B. P_a of the curve II will be transferred vertically on the curve I.

As shown on the curve I, according to Oyagi's method, the maximum amount of Bound Water will be seen as about 49% of the water-content (at the blue point) and the minimum amount of Bound Water will be seen as about 27% of the water-content (at constant point by drying at 30°C). According to Hatschek's method, the maximum amount of Bound Water will be seen as about 35% of the water-content. O. B. P_a, O. C. P_a and H. B. P_a of the curve I are situated on the curve of which the vapour tension begins to decrease gradually.

The curves III and IV in Fig. 8 are curves of the water-content—vapour tension for Sandfish and Squid respectively.

The amount of Bound Water of those samples by Oyagi's method which were written from the 5th to the 8th columns in Table 9 are shown as O. B. P_b, O. C. P_b and O. C. P_c on the curves III and IV respectively. As seen in the curves III and IV, the vapour tension decreases suddenly from the blue turning point (B. P.) and it decreases suddenly from the constant point (C. P.), as well as in the case of Atka Mackerel meat above.

In Fig. 9-1 the curve I is shown as the curve of the water-content—water-

activity of fresh Atka Mackerel meat containing no cobaltous chloride, and the curve II is shown as Atka Mackerel meat containing cobaltous chloride.

In the case of Atka Mackerel meat containing cobaltous chloride, the boundary of Bound Water and Free Water at the blue turning point (H. B. P_a) is seen as 0.65 of the activity of water in the fish muscle. But the value of the amount of Bound Water on the curve II will be determined as the water-content corresponding to 0.8—0.83 of the water-activity when the point of H. B. P_a of the curve II will be transferred horizontally on the curve I in order to show the amount of Bound Water in the fresh Atka Mackerel containing no cobaltous chloride.

O. B. P_a and O. C. P_a on the curve I show the amount of Bound Water (g') per gm of the dried matter containing cobaltous chloride, therefore the points of O. B. P_a and O. C. P_a must be transferred to the upper positions on the same curve respectively.

In general, according to Oyagi's method the maximum amount of Bound Water will be determined as the water-content corresponding to 0.95—0.9 of the water-activity "a" at the point of B. P. and the minimum amount of Bound Water will be determined as the water-content corresponding to 0.85—0.8 of the water-activity at the point of C. P.

In the case of Oyagi's method and Hatschek's method the points of O. B. P_a, O. C. P_a and H. B. P_a are situated in the range of 1.0—0.8 of the water-activity on the curve I.

Here, the author knows that the values of the amount of Bound Water which were estimated by cobaltous chloride methods do not agree with the value of the amount of the molecular Bound Water, but rather agree with the approximate value of the amount of the colloidal Bound Water as in the case of gelatine. That is to say, according to the cobaltous chloride method, we can not estimate the amount of Bound Water when the water-activity is below 0.8—0.7, even if we employ the value at blue turning point or at apparent constant point in the course of drying.

The author has the same conclusion on the curve III of Sandfish meat and the curve IV of Squid as in the case of Atka Mackerel meat.

The curve I′ (dotted line) of Fig. 9-1 shows the curve of the theoretically calculated values for the Atka Mackerel meat containing a known quantity of cobaltous chloride from the curve I of the same fresh meat as well as in the case of gelatine. These calculated values are shown from the 11th to the 14th

columns of Table 10.

In this case, the quantity of cobaltous chloride per gm of the dried matter of Atka Mackerel meat containing cobaltous chloride is 0.221 gm, therefore 2.18×10^{-3} Mol of cobaltous chloride is equivalent to 1 gm of dried fish meat. The amount of hydrated water to cobaltous chloride at each water-activity is calculated by the equation (2) as well as in the case of the sample of gelatine above.

As shown in Fig. 9-1, the curve I′ which was theoretically formed as above stated, agrees perfectly with the curve II which was observed by experiments. The ratio of the theoretical value to the observed value was 1.092 on the average. But as described in the case of the sample of gelatine, the theoretical curve I′ does not fit with the actual system of cobaltous chloride and water, because when we compare the observed value with the theoretical value in the system of water and cobaltous chloride, the observed values for the water-content of the system are determined as lower water-activities in the same water-content. Here supposing that there is a curve which fits the practical case, the author calls it as the curve I″. Therefore the curve of the observed value for the fish meat containing cobaltous chloride (the curve II) is situated under the supposed curve, I″. For this reason, not all of the molecules of the added cobaltous chloride hydrate with the water in the fish meat muscle by the presence of Bound Water, but a part of the added cobaltous chloride precipitates as solid, and the remainder of it hydrates with water in fish meat muscle in the predetermined quantity. The hydrated water with cobaltous chloride indicates the same water-activity of the water which is hydrated in fish meat muscle.

(C) The comparison of the results by the electric resistance with the results by cobaltous chloride method.

As seen in the relation between the water-content in Atka Mackerel and Squid meat and electric resistance of 50 cycles which is shown in Table 12-1, 12-2 and Fig. 10-1, 10-2, as well as in the case of gelatine, the electric resistance decreases more or less in the initial decreasing of the water-content of the curve, and begins to increase at 55～60% of the water-content, and it increases more and more with the decreasing of the water-content afterwards. Below 20% of the water-content, the relation between the water-content and the logarithm of electric resistance shows a straight line, and the electric resistance increases suddenly at that water-content.

That is to say, the electric resistance shows gradual increasing at the point of B. P. by Oyagi's and Hatschek's method's, and the point of C. P. by Oysgi's

method is situated before the sudden increasing of electric resistance.

These facts will be understood from the reason that Bound Water does not act as a solvent for electrolytes, and the value given at C. P. by cobaltous chloride methods is probably colloidal Bound water, as well as in the case of gelatine.

The decreasing of electric resistance at initial decreasing of water-content is admitted clearly in the case of Atka Mackerel meat in Fig. 9-1, when the pole-distances are 1.5, 2.0 and 3.0 cm.

These facts will also be understood as well as in the case of gelatine from the reason that the concentraion of salt solution in fish meat muscle increases in accordance with the decreasing of Free Water and the so called "water-channel" will be formed in the tissue of fish meat by the shrinking of fish meat in the initial course of drying.

2. Conclusions on the comparison of estimation of Bound Water by the cobaltous chloride methods with the vapour tension and the method by electric resistance.

As the examinations of the estimation of the amount of Bound Water, the author has estimated the amount of Bound Water in gelatine and fish meat muscle by the cobaltous chloride methods, the vapour tension method, and the method by electric resistance of 50 cycles, and these results obtained were compared with each other, and the following conclusions were obtained.

(1) In the case of the estimation of Bound Water in the samples by the cobaltous chloride methods (Oyagi's and Hatschek's methods), the author was able to estimate the amount of Bound Water at the point of B. P. (the blue turning point) and C. P. (the point of apparent constant weight in the drying at 30°C) on the basis of ideas for the Bound Water. The author has called the water-content at B. P. the maximum amount of Bound Water and the water-content at C. P. the minimum amount of Bound Water.

(2) When the amount of Bound Water in gelatine and fish meat was estimated by the cobaltous chloride methods, and these results were compared with the values on the curve of water-content—water-activity obtained by the vapour tension method, the amounts of Bound Water per gm of the dried matter of the sample at the points of H. B. P. and H. C. P. by Hatschek's method and O. C. P. by Oyagi's method were ascertained to be the water-content in the sample corresponding to above 0.8~0.7 of the water-activity, and these values will give the probable value which has been considered before as the amount of colloidal Bound Water,

and the amount of water (gm) per gm of the dried matter of samples (containing cobaltous chloride) at the points of O. B. P′. and O. C. P′. will give also the value of the amount of colloidal Bound Water.

(3) In the cobaltous chloride methods, cobaltous chloride which was added to the samples or which penetrated into the sample decreases the activity of water in the sample.

The degree of decreasing of the water-activity is different from the activity of water hydrated with the sample which is added with cobaltous chloride. (That is to say, it is different from binding strength of sample with water.) In this case, when we suppose that water which is hydrated with cobaltous chloride shows the same water-activity as water which is hydrated with the sample, the hydration of cobaltous chloride which is added to the sample is restricted in accordance with the increasing of binding strength of the sample with water, but all the quantity of the added cobaltous chloride does not take a part of the hydration of water in the sample.

(4) In the results of the estimation of the amount of Bound Water, the electric resistance decreases in the range of from 80% to 50~60%, and it begins increase at about 50% of water-content. The electric resistance gradually increases at the point of B. P. which was considered to be shown as the maximum amount of Bound Water (the water-content 50~30%) by the cobaltous chloride method, and it increases rapidly at the point of C. P. which was considered to be the minimum amount of Bound Water (30~20%) by the same method. At below 20% of the water-content, the relation between the increasing of electric resistance and the water-content showed a logarithmic straight line.

(5) From the results of the estimation of the amount of Bound Water in gelatine and fish meat by the cobaltous chloride methods, the following facts are shown.

(a) The amount of Bound Water per gm of dried matter is almost the same in the sample (gelatine) of 0.5~0.1 gm in size in the author's experiment.

(b) The amount of Bound Water in the air dried gelatine is greater than the bone dried gelatine.

(c) The amount of Bound Water is different in the kinds of the same sample.

(d) Oyagi's method gives a greater amount of Bound water than the Hatschek's method.

(e) The greater the concentration of gel of gelatine increases, the less the amount of Bound Water becomes.

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